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(71)Applicant : FUJI PHOTO FILM CO LTD

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(72)Inventor : AOSO TOSHIKI

(54) NEGATIVE TYPE RESIST COMPOSITION FOR ELECTRON BEAM OR X-RAY**(57)Abstract:**

PROBLEM TO BE SOLVED: To solve the problem of a performance enhancing technique in the microfabrication of a semiconductor device using electron beams or X-rays and to provide a negative type chemical amplification type resist composition for electron beams or X-rays which satisfies characteristics such as sensitivity and resolution in the use of electron beams or X-rays, resist shape, development defects, applicability and solubility in a solvent.

SOLUTION: The negative type chemical amplification type resist composition contains a compound which generates an acid and/or a radical species when irradiated with electron beams or X-rays, an alkali-soluble resin, a crosslinker which causes crosslinking under the acid and a solvent.

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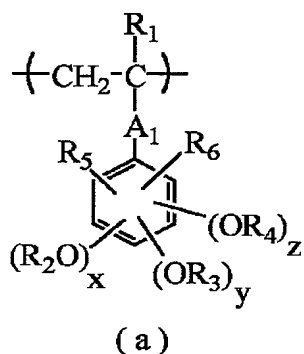
CLAIMS

[Claim(s)]

[Claim 1] (A) The compound which generates an acid and/or a radical kind by the exposure of an electron ray or an X-ray, (B) -- the water which has at least one unsaturated bond in which a polymerization is possible by the acid and/or the radical -- insoluble -- resin meltable in an alkali water solution -- (C) The solvent of (the cross linking agent which produces the resin of B) and bridge formation, and (D) following (a) is contained 40 to 90% of the weight to all solvents according to an operation of an acid. (Solvent a) propylene-glycol-monomethyl-ether acetate which contains the solvent of (b) ten to 60% of the weight to all solvents, Propylene-glycol-monomethyl-ether propionate, 3-methoxy methyl propionate, 3-methoxy ethyl propionate, 3-ethoxy methyl propionate, At least one sort of solvent (b) propylene glycol monomethyl ether chosen from 3-ethoxy ethyl propionate, The negative-resist constituent for an electron ray or X-rays characterized by containing at least one sort of solvents chosen from the propylene glycol monoethyl ether, methyl lactate, ethyl lactate, and diacetone alcohol.

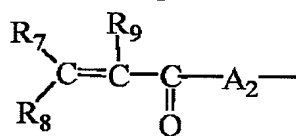
[Claim 2] (B) The electron ray according to claim 1 or the negative-resist constituent for X-rays characterized by the resin of a component being resin containing the repeat unit of a general formula (a).

[Formula 1]

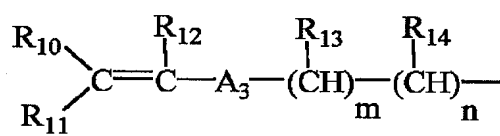


R1 expresses among a formula the alkyl group or halo alkyl group which may have the hydrogen atom, the halogen atom, the cyano group, and the substituent. R2–R4 express the alkyl group and cycloalkyl radical which may have which radical of a hydrogen atom, a general formula (b), (c), or (d), and the substituent, an aryl group, an aralkyl radical, or an acyl group. even if R5 and R6 are the same, they may differ from each other, and they express the alkyl group and cycloalkyl radical which may have a hydrogen atom, hydroxyl, the halogen atom, the cyano group, or the substituent, an alkenyl radical, an aralkyl radical, or an aryl group.

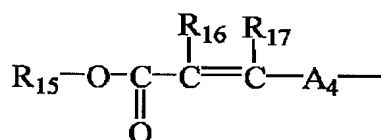
[Formula 2]



(b)



(c)



(d)

R7-R12, and R16 and R17 express among a formula the alkyl group or halo alkyl group which may have the hydrogen atom, the halogen atom, the cyano group, and the substituent. The alkyl group and alkoxy group which may have R13, R14, *****, the halogen atom, the hydroxy group, and the substituent, and an acyloxy radical are expressed. R15 expresses the alkyl group and cycloalkyl radical which may have the hydrogen atom and the substituent, an aralkyl radical, or an aryl group. A1 expresses the divalent alkylene group and alkenylene group which may have single bond and a substituent, a cyclo alkylene group, an arylene radical or $-O-$, $-SO_2-$, $-O-CO-R_{20}-$, $-CO-O-R_{21}-$, and $-CO-N(R_{22})-R_{23}-$. even if R20, R21, and R23 are the same, they may differ from each other, and they express the divalent alkylene group and alkenylene group which may have a substituent [single bond or ether structure ester structure, amide structure, urethane structure, or ureido structure], a cyclo alkylene group, and an arylene radical. R22 expresses the alkyl group and cycloalkyl radical which may have the hydrogen atom and the substituent, an aralkyl radical, or an aryl group. A2 expresses single bond, $-O-R_{21}-$, and $-N(R_{22})-R_{23}-$. A3 expresses the arylene radical which may have a substituent [single bond and $-SO_2-$ or alkylene structure]. A4 expresses the divalent alkylene group and cyclo alkylene group which may have single bond and a substituent, an arylene radical, $-O-$, $-SO_2-$, $-CO-$, and $-CO-O-R_{21}-$. z expresses x, y and 0, or 1, and m and n express 0 or one or more integers. However, at least one has the radical of a general formula (b), (c), or (d) among a general formula (a). Moreover, 2 of R2-R4 or one of R2-the R4, R5, or R6 may join together, and a ring may be formed.

[Claim 3] Furthermore, the electron ray according to claim 1 or 2 or the negative-resist constituent for X-rays characterized by containing the compound which has at least one unsaturated bond in which a polymerization is possible by the (E) acid and/or the radical.

[Claim 4] Furthermore, the electron ray according to claim 1 to 3 or the negative-resist constituent for X-rays characterized by containing (F) organic base nature compound.

[Claim 5] (A) The electron ray according to claim 1 to 4 or the negative-resist constituent for X-rays with which the compound of a component is characterized by being chosen from the sulfonate compound of sulfonium or iodonium.

[Claim 6] (A) The electron ray according to claim 1 to 4 or the negative-resist constituent for X-rays with which the compound of a component is characterized by being the sulfonate compound of N-hydroxy imide, or a disulfo nil diazomethane compound.

[Claim 7] (C) The electron ray according to claim 1 to 6 or the negative-resist constituent for X-rays with which the cross linking agent of a component is characterized by being hydroxymethyl-izing and the phenolic compound which methylated [alkoxy-] or methylated [acyloxy-].

[Claim 8] (C) The electron ray according to claim 1 to 6 or the negative-resist constituent for X-rays characterized by the cross linking agent of a component being the melamine compound which methylated [alkoxy-] or methylated [acyloxy-], resin, an urea compound, or resin.

[Claim 9] The electron ray according to claim 1 to 8 or the negative-resist constituent for X-rays characterized by being a constituent for carrying out electron beam irradiation under the acceleration voltage conditions of 75 or more keVs.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the negative-resist constituent used suitable for super-micro lithography processes, such as a VLSI and manufacture of a high capacity microchip, or other photofabrication processes. It is related with the negative-resist constituent which can be used especially suitable for micro processing of the semiconductor device using high energy lines, such as an electron ray, in more detail about the negative-mold photoresist constituent which was made highly minute using the X-ray, the electron ray, etc. and which can carry out pattern formation.

[0002]

[Description of the Prior Art] the integrated circuit is raising the degree of integration increasingly, and consists of the line breadth below a half micron in manufacture of semi-conductor substrates, such as a VLSI, -- processing of a detailed pattern has overly come to be needed. In order to fulfill the need, operating wavelength of the aligner used for photolithography is short-wave-ized increasingly, and by the time far-ultraviolet light and excimer laser light (XeCl, KrF, ArF, etc.) are examined, now, it will become. Still more detailed pattern formation has come [furthermore, / by the electron ray or the X-ray] to be considered.

[0003] Especially as for an electron ray or an X-ray, the next generation or development of the negative resist which is positioned as a generation's pattern formation technique one after another, and can attain high sensitivity and a high resolving and rectangle profile configuration is desired. Electron-beam lithography supplies energy to a compound in the atom with which the accelerated electron ray constitutes a resist ingredient, and the process in which collision dispersion is caused, occurs the reaction of a resist ingredient, and makes an image form. Although rectilinear-propagation nature increases by using the high-accelerated

electron ray, the effect of electronic dispersion decreases and the pattern formation of a rectangle configuration becomes possible by high resolving, on the other hand, the permeability of an electron ray will become high and sensibility will fall. Thus, in electron-beam lithography, it was a technical problem how sensibility, and definition and a resist configuration may be compatible in this by having the relation of a trade-off. As a resist ingredient to these, it is the purpose which raises sensibility, and the chemistry magnification mold resist which mainly used the acid catalyzed reaction is used, and the chemistry magnification setup-of-tooling product which consists of alkali fusibility resin, an acid generator, and an acid cross linking agent is effectively used as a principal component to negative resist.

[0004] Various alkali fusibility resin has been conventionally proposed to a negative chemistry magnification mold resist. To patent No. 2505033, JP,3-170554,A, and JP,6-118646,A, for example, novolak mold phenol resin, The polyvinyl phenol resin which narrowed the molecular weight distribution to JP,7-311463,A and JP,8-292559,A, The phenol resin changed into JP,3-87746,A and JP,8-44061,A in part by hydrogenation at cyclic alcohol structure, The resin which protected a part of OH radical of a polyvinyl phenol by the alkyl group to JP,7-295200,A and JP,8-152717,A, The polyvinyl phenol resin which has a protective group inactive in acids, such as an acyl group, in JP,8-339086,A, The polyvinyl phenol resin copolymerized with styrene in JP,6-67431,A and JP,10-10733,A, Acrylate monomers, the copolymerized polyvinyl phenol resin, and the resin which has a carboxy group are further indicated by JP,9-166870,A (meta) at JP,8-240911,A.

[0005] About an acid generator, to JP,8-3635,B, moreover, an organic halogenated compound, The aromatic compound, JP,4-367864,A which Br and Cl permuted by JP,2-52348,A, The aromatic compound which has the alkyl group which Br and Cl permuted by JP,4-367865,A, and an alkoxy group, To JP,2-150848,A and JP,6-199770,A, iodonium, To a sulfonium compound and JP,3-87746,A, a haloalkane sulfonate compound, To JP,4-210960,A and JP,4-217249,A, a diazo disulfon compound, To a diazo sulfone compound and JP,4-336454,A, or Br, I permutation alkyl triazine compound, To JP,4-291258,A, a sulfonamide, a sulfone imide compound, To JP,4-291259,A, the sulfonic-acid compound of a polyhydric phenol, To JP,4-291260,A, JP,4-291261,A, and JP,6-202320,A, a naphthoquinonediazide-4-sulfonate compound, The benzyl sulfonate compound etc. is indicated by an N-oxy-imide sulfonate compound and U.S. Pat. No. 5344742 at JP,5-210239,A at a disulfon compound and JP,6-236024,A.

[0006] As opposed to an acid cross linking agent Furthermore, JP,3-75652,A, JP,5-181277,A, To JP,7-146556,A, a methoxymethyl melamine compound, JP,4-281455,A, The compound which has an alkoxy methyl ether radical in JP,5-232702,A and JP,6-83055,A, To JP,5-281715,A, an oxazine compound, JP,5-134412,A, The alkoxy methyl URIRU compound given in JP,1-293339,A besides a trioxane compound etc. is indicated by the aromatic compound and JP,6-194838,A which have an alkoxyalkyl group in JP,6-3825,A. However, also in which combination of these compounds, it is difficult to obtain sufficient high sensitivity under the electron beam irradiation under high acceleration voltage conditions, and X-ray irradiation, and it had become a technical problem to make it compatible on the level with which may be satisfied of sensibility, resolution, and a resist configuration. Furthermore, control of a development defect, good spreading nature (homogeneity of a spreading side), and good solvent solubility (deposit prevention by preservation with the passage of time) were also desired.

[0007]

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is solving the technical

problem of the improvement technique in the engine performance in micro processing of the semiconductor device which uses an electron ray or an X-ray, and is offering the negative-mold chemistry multiplier system resist constituent for an electron ray or X-rays with which it is satisfied of sensibility, resolution, a resist configuration, a development defect, spreading nature, and the property of solvent solubility to use of an electron ray or an X-ray. Furthermore, it is offering the negative-mold chemistry multiplier system resist constituent for an electron ray or X-rays which can respond to next-generation EB irradiation equipment (EB block exposure machine or EB stepper (serially contraction projection exposure machine) who aimed at improvement in a throughput) which suited the mass-production nature of a semiconductor device and in which high sensitivity's is shown.

[0008]

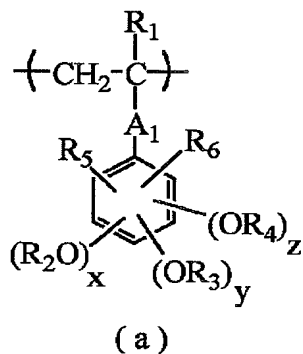
[Means for Solving the Problem] this invention person etc. reached [being splendidly attained because the purpose of this invention uses the following specific constituents, and] a header and this invention, as a result of inquiring wholeheartedly with careful attention to many above-mentioned properties. That is, this invention is the following configuration.

[0009] (1) The compound which generates an acid and/or a radical kind by the exposure of the (A) electron ray or an X-ray, (B) — the water which has at least one unsaturated bond in which a polymerization is possible by the acid and/or the radical — insoluble — resin meltable in an alkali water solution — (C) The solvent of (the cross linking agent which produces the resin of B) and bridge formation, and (D) following (a) is contained 40 to 90% of the weight to all solvents according to an operation of an acid. (Solvent a) propylene-glycol-monomethyl-ether acetate which contains the solvent of (b) ten to 60% of the weight to all solvents, Propylene-glycol-monomethyl-ether propionate, 3-methoxy methyl propionate, 3-methoxy ethyl propionate, 3-ethoxy methyl propionate, At least one sort of solvent (b) propylene glycol monomethyl ether chosen from 3-ethoxy ethyl propionate, The negative-resist constituent for an electron ray or X-rays characterized by containing at least one sort of solvents chosen from the propylene glycol monoethyl ether, methyl lactate, ethyl lactate, and diacetone alcohol.

[0010] (2) Negative-resist constituent for an electron ray or X-rays given in the above (1) characterized by the resin of the (B) component being resin containing the repeat unit of a general formula (a).

[0011]

[Formula 3]

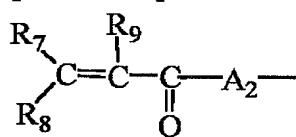


[0012] R1 expresses among a formula the alkyl group or halo alkyl group which may have the hydrogen atom, the halogen atom, the cyano group, and the substituent. R2-R4 express the alkyl group and cycloalkyl radical

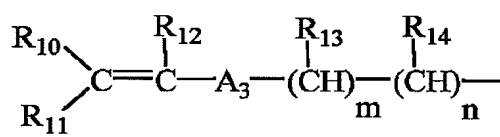
which may have which radical of a hydrogen atom, a general formula (b), (c), or (d), and the substituent, an aryl group, an aralkyl radical, or an acyl group. even if R5 and R6 are the same, they may differ from each other, and they express the alkyl group and cycloalkyl radical which may have a hydrogen atom, hydroxyl, the halogen atom, the cyano group, or the substituent, an alkenyl radical, an aralkyl radical, or an aryl group.

[0013]

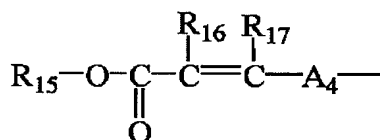
[Formula 4]



(b)



(c)



(d)

[0014] R7-R12, and R16 and R17 express among a formula the alkyl group or halo alkyl group which may have the hydrogen atom, the halogen atom, the cyano group, and the substituent. The alkyl group and alkoxy group which may have R13, R14, *****, a halogen atom, hydroxyl, and a substituent, and an acyloxy radical are expressed. R15 expresses the alkyl group and cycloalkyl radical which may have the hydrogen atom and the substituent, an aralkyl radical, or an aryl group. A1 expresses the divalent alkylene group and alkenylene group which may have single bond and a substituent, a cyclo alkylene group, an arylene radical or -O-, -SO2-, -O-CO-R20-, -CO-O-R21-, and -CO-N(R22)-R23-. even if R20, R21, and R23 are the same, they may differ from each other, and they express the divalent alkylene group and alkenylene group which may have a substituent [single bond or ether structure ester structure, amide structure, urethane structure, or ureido structure], a cyclo alkylene group, and an arylene radical. R22 expresses the alkyl group and cycloalkyl radical which may have the hydrogen atom and the substituent, an aralkyl radical, or an aryl group. A2 expresses single bond, -O-R21-, and -N(R22)-R23-. A3 expresses the arylene radical which may have a substituent [single bond and -SO2- or alkylene structure]. A4 expresses the divalent alkylene group and cyclo alkylene group which may have single bond and a substituent, an arylene radical, -O-, -SO2-, -CO-, and -CO-O-R21-. z expresses x, y and 0, or 1, and m and n express 0 or one or more integers. However, at least one has the radical of a general formula (b), (c), or (d) among a general formula (a). Moreover, 2 of R2-R4 or one of R2-the R4, R5, or R6 may join together, and a ring may be formed.

[0015] (3) The negative-resist constituent for an electron ray or X-rays the above (1) characterized by containing the compound which furthermore has at least one unsaturated bond in which a polymerization is possible by the (E) acid and/or the radical, or given in (2).

[0016] (4) The negative-resist constituent for an electron ray or X-rays given in either of aforementioned (1) - (3) characterized by furthermore containing (F) organic base nature compound.

[0017] (5) Negative-resist constituent for an electron ray or X-rays given in either of aforementioned (1) - (4) to which the compound of the (A) component is characterized by being chosen from the sulfonate

compound of sulfonium or iodonium.

[0018] (6) Negative-resist constituent for an electron ray or X-rays given in either of aforementioned (1) – (4) to which the compound of the (A) component is characterized by being the sulfonate compound of N-hydroxy imide, or a disulfo nil diazomethane compound.

[0019] (7) Negative-resist constituent for an electron ray or X-rays given in either of aforementioned (1) – (6) to which the cross linking agent of the (C) component is characterized by being hydroxymethyl-izing and the phenolic compound which methylated [alkoxy-] or methylated [acyloxy-].

[0020] (8) Negative-resist constituent for an electron ray or X-rays given in either of aforementioned (1) – (6) characterized by the cross linking agent of the (C) component being the melamine compound which methylated [alkoxy-] or methylated [acyloxy-], resin, an urea compound, or resin.

[0021] (9) The negative-resist constituent for an electron ray or X-rays given in either of aforementioned (1) – (8) characterized by being a constituent for carrying out electron beam irradiation under the acceleration voltage conditions which are 75 or more keVs.

[0022]

[Embodiment of the Invention] Hereafter, the compound used for this invention is explained to a detail.

(1) The resin of resin this invention (B) of this invention (B) It is insoluble and is resin meltable in an alkali water solution. the water which has at least one unsaturated bond in which a polymerization is possible by the acid and/or the radical — Preferably Phenol novolak resin, polyvinyl phenol resin, The copolymer which has the structural unit of the vinyl phenol origin, and the resin obtained by protecting or embellishing a part of polyvinyl phenol resin, The resin which permuted a part or all of a phenolic group that have a phenol frame (meta), such as an acrylate polymer, by the radical which has the unsaturated bond in which a polymerization is possible by the acid and/or the radical can be used widely. The resin of the phenol system containing the repeat structural unit preferably expressed with the above-mentioned general formula (a) can be mentioned.

[0023] The inside of a general formula (a) and R1 express the alkyl group or halo alkyl group which may have the hydrogen atom, the halogen atom, the cyano group, and the substituent. R2–R4 express the alkyl group and cycloalkyl radical which may have which radical of a hydrogen atom, the above-mentioned general formula (b), (c), or (d), and the substituent, an aryl group, an aralkyl radical, or an acyl group. even if R5 and R6 are the same, they may differ from each other, and they express the alkyl group and cycloalkyl radical which may have a hydrogen atom, hydroxyl, the halogen atom, the cyano group, or the substituent, an alkenyl radical, an aralkyl radical, or an aryl group.

[0024] R7–R12, and R16 and R17 express the alkyl group or halo alkyl group which may have the hydrogen atom, the halogen atom, the cyano group, and the substituent. The alkyl group and alkoxy group which may have R13, R14, *****, a halogen atom, hydroxyl, and a substituent, and an acyloxy radical are expressed. R15 expresses the alkyl group and cycloalkyl radical which may have the hydrogen atom and the substituent, an aralkyl radical, or an aryl group.

[0025] A1 expresses the divalent alkylene group and alkenylene group which may have single bond and a substituent, a cyclo alkylene group, an arylene radical or –O–, –SO₂–, –O–CO–R₂₀–, –CO–O–R₂₁–, and –CO–N(R₂₂)–R₂₃–. even if R₂₀, R₂₁, and R₂₃ are the same, they may differ from each other, and they express the divalent alkylene group and alkenylene group which may have a substituent [single bond or ether structure ester structure, amide structure, urethane structure, or ureido structure], a cyclo alkylene

group, and an arylene radical.

[0026] R22 expresses the alkyl group and cycloalkyl radical which may have the hydrogen atom and the substituent, an aralkyl radical, or an aryl group. A2 expresses single bond, $-O-R21-$, and $-N(R22)-R23-$. A3 expresses the arylene radical which may have a substituent [single bond and $-SO2-$ or alkylene structure]. A4 expresses the divalent alkylene group and cyclo alkylene group which may have single bond and a substituent, an arylene radical, $-O-$, $-SO2-$, $-CO-$, and $-CO-O-R21-$.

[0027] z expresses x, y and 0, or 1, and m and n express 0 or one or more integers. However, at least one has the radical of a general formula (b), (c), or (d) among a general formula (a). Moreover, 2 of R2-R4 or one of R2-the R4, R5, or R6 may join together, and a ring may be formed.

[0028] Moreover, as an alkyl group of R1-R17, and R22, it is the alkyl group of 1-8 carbon numbers, for example, and, specifically, a methyl group, an ethyl group, a propyl group, n-butyl, sec-butyl, a hexyl group, a 2-ethylhexyl radical, and an octyl radical can be mentioned preferably.

[0029] A monocycle mold is sufficient as R2-R6, R₁₅, and the cycloalkyl radical of R22, and a polycyclic mold is sufficient as them. As a monocycle mold, for example, the cyclo propyl group of 3-8 carbon numbers, a cyclopentyl group, and a cyclohexyl radical can be mentioned preferably. As a polycyclic mold, for example, an adamantyl radical, a norbornyl radical, an isoboronyl radical, a JISHIKURO pentyl radical, a-PINERU radical, a tricyclo deca nil radical, etc. can be mentioned preferably.

[0030] As an alkenyl radical of R5 and R6, it is the alkenyl radical of 2-8 carbon numbers, for example, and, specifically, a vinyl group, an allyl group, a butenyl group, and a cyclohexenyl group can be mentioned preferably.

[0031] As an aryl group of R2-R6, and R15 and R22, it is the aryl group of 6-15 carbon numbers, for example, and, specifically, a phenyl group, a tolyl group, a dimethylphenyl radical, 2 and 4, 6-trimethyl phenyl radical, a naphthyl group, an anthryl radical, etc. can be mentioned preferably. As R2-R6, and an aralkyl radical of R15 and R22, it is the aralkyl radical of 7-12 carbon numbers, for example, and, specifically, benzyl, a phenethyl radical, a naphthyl methyl group, etc. can be mentioned preferably.

[0032] As R1, R7-R12, and a halo alkyl group of R16 and R17, it is the halo alkyl group of 1-4 carbon numbers, for example, and a chloro methyl group, a chloro ethyl group, a chloropropyl radical, a chlorobutyl radical, a bromomethyl radical, a BUROMO ethyl group, etc. can specifically be mentioned preferably. As an acyl group of R2-R4, it is the acyl group of 1-10 carbon numbers, for example, and a formyl group, an acetyl group, a propanoyl radical, a butanoyl radical, a pivaloyl radical, benzoyl, etc. can be mentioned preferably.

[0033] As an alkoxy group of R13 and R14, it is the alkoxy group of 1-8 carbon numbers, for example, and a methoxy group, an ethoxy radical, a propoxy group, a butoxy radical, etc. can be mentioned preferably. As an acyloxy radical, it is the acyloxy radical of 1-10 carbon numbers, for example, and an acetoxyl radical, a propanoyloxy radical, a benzoyloxy radical, etc. can be mentioned preferably.

[0034] As A1, A4, and an alkylene group of R20, R21, and R23, it is the alkylene group of 1-8 carbon numbers, for example, and a methylene group, ethylene, a propylene radical, a butylene radical, a hexylene radical, an octylene radical, etc. can be mentioned preferably. As an alkenylene group of A1, R20, R21, and R23, it is the alkenylene group of 2-6 carbon numbers, for example, and an ETENIREN radical, a pro PENIREN radical, a butenylene radical, etc. can be mentioned preferably.

[0035] As A1, A4, and a cyclo alkylene group of R20, R21, and R23, it is the cyclo alkylene group of 5-8

carbon numbers, for example, and a cyclo pentene radical, a cyclo hexylene radical, etc. can be mentioned preferably. As A1, A3, A4, and an arylene radical of R20, R21, and R23, it is the arylene radical of 6–12 carbon numbers, for example, and a phenylene group, a tolylene radical, a xylylene radical, a naphthylene radical, etc. can be mentioned preferably.

[0036] furthermore, as a substituent permuted by these radicals What [has active hydrogen, such as the amino group, an amide group, an ureido radical, a urethane group, hydroxyl, and a carboxyl group] a halogen atom (a fluorine atom, a chlorine atom, a bromine atom, iodine atom) and an alkoxy group (a methoxy group --) thioether radicals, such as an ethoxy radical, a propoxy group, and a butoxy radical, and an acyl group (an acetyl group --) Acyloxy radicals (an acetoxyl radical, a propanoyloxy radical, benzoyloxy radical, etc.), such as a propanoyl radical and benzoyl, alkoxy carbonyl groups (a methoxycarbonyl group, an ethoxycarbonyl radical, propoxy carbonyl group, etc.), a cyano group, a nitro group, etc. are mentioned. What has active hydrogen, such as an amino group, hydroxyl, and a carboxyl group, especially is desirable.

[0037] Moreover, as a ring which 2 of R2–R4 or one of R2–the R4, R5, or R6 combined and formed, four to 7 membered–ring containing oxygen atoms, such as a benzofuran ring, a benzodioxo Norian ring, and a benzopyran ring, is mentioned.

[0038] Although the resin of this invention (B) may be resin which consists only of a repeat structural unit of a general formula (a), it is the purpose which raises the engine performance of the negative resist of this invention further, and may carry out copolymerization of other polymerization nature monomers.

[0039] What is shown below is contained as a copolymerization monomer which can be used. For example, it is the compound which has one addition polymerization nature unsaturated bond chosen from acrylic ester other than the above, acrylamides, methacrylic ester, methacrylamide, an allyl compound, vinyl ether, vinyl ester, styrene, and crotonic–acid ester.

[0040] Specifically For example, acrylic ester, for example, alkyl (carbon atomic number of alkyl group has desirable thing of 1–10) acrylate for example, a methyl acrylate, an ethyl acrylate, and acrylic–acid propyl -- Acrylic–acid t–butyl, acrylic–acid amyl, acrylic–acid cyclohexyl, Acrylic–acid ethylhexyl, acrylic–acid octyl, acrylic–acid–t–octyl, Chlorethyl acrylate, 2–hydroxyethyl acrylate 2, 2–dimethyl hydroxypropyl acrylate, 5–hydroxy pentyl acrylate, trimethylol propane monoacrylate, Aryl acrylate (for example, phenyl acrylate etc.), such as pentaerythritol monoacrylate, glycidyl acrylate, benzyl acrylate, furfuryl acrylate, and tetrahydrofurfuryl acrylate;

[0041] Methacrylic ester, for example, alkyl (carbon atomic number of alkyl group has desirable thing of 1–10) methacrylate for example, methyl methacrylate, ethyl methacrylate, and propyl methacrylate -- Isopropyl methacrylate, t–butyl methacrylate, amyl methacrylate, Hexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, KURORU benzyl methacrylate, octyl methacrylate, 2–hydroxyethyl methacrylate, 4–hydroxy butyl methacrylate, 5–hydroxy pentyl methacrylate, 2 and 2–dimethyl–3–hydroxypropyl methacrylate, trimethylol propane mono–methacrylate, Pentaerythritol mono–methacrylate, glycidyl methacrylate, Aryl methacrylate (for example, phenyl methacrylate, cresyl methacrylate, naphthyl methacrylate, etc.), such as furfuryl methacrylate and tetrahydrofurfuryl methacrylate;

[0042] Acrylamides, for example, acrylamide, N–alkyl acrylamide (as an alkyl group), there are the thing of the carbon atomic numbers 1–10, for example, a methyl group, an ethyl group, a propyl group, butyl, t–butyl,

a heptyl radical, an octyl radical, a cyclohexyl radical, benzyl, a hydroxyethyl radical, benzyl, etc. N-aryl acrylamide (as an aryl group, there are a phenyl group, a tolyl group, a nitrophenyl group, a naphthyl group, a cyanophenyl radical, a hydroxyphenyl radical, a carboxyphenyl radical, etc., for example.) N and N-dialkyl acrylamide (as an alkyl group) there are the thing of the carbon atomic numbers 1-10, for example, a methyl group, an ethyl group, butyl, an isobutyl radical, an ethylhexyl radical, a cyclohexyl radical, etc. N and N-diaryl acrylamide (as an aryl group, there is a phenyl group etc., for example.) N-methyl-N-phenyl acrylamide, N-hydroxyethyl-N-methylacrylamide, N-2-acetamidoethyl-N-acetyl acrylamide, etc.;

[0043] Methacrylamide, for example, methacrylamide, N-alkyl methacrylamide (as an alkyl group) there are the thing of the carbon atomic numbers 1-10, for example, a methyl group, an ethyl group, t-butyl, an ethylhexyl radical, a hydroxyethyl radical, a cyclohexyl radical, etc. N-aryl methacrylamide (there is a phenyl group etc. as an aryl group.) N and N-dialkyl methacrylamide (there are an ethyl group, a propyl group, butyl, etc. as an alkyl group.) N and N-diaryl methacrylamide (there is a phenyl group etc. as an aryl group.) N-hydroxyethyl-N-methyl methacrylamide, N-methyl-N-phenyl methacrylamide, N-ethyl-N-phenyl methacrylamide etc.; An allyl compound For example, allyl ester, allyloxy ethanol (for example, an acetic-acid allyl compound, allyl caproate, a caprylic-acid allyl compound, a lauric-acid allyl compound, a palmitic-acid allyl compound, a stearin acid allyl compound, allyl benzoate, an acetoacetic-acid allyl compound, a lactic-acid allyl compound, etc.), etc.;

[0044] vinyl ether (for example, hexyl vinyl ether --), for example, alkyl vinyl ether Octyl vinyl ether, DESHIRU vinyl ether, ethylhexyl vinyl ether, Methoxy ethyl vinyl ether, ethoxyethyl vinyl ether, KURORU ethyl vinyl ether, The 1-methyl -2, 2-dimethyl propyl vinyl ether, 2-ethyl butyl vinyl ether, Hydroxyethyl vinyl ether, diethylene-glycol vinyl ether, Dimethylaminoethyl vinyl ether, diethylamino ethyl vinyl ether, Butylamino ethyl vinyl ether, benzyl vinyl ether, tetrahydrofurfuryl vinyl ether, etc., Vinyl aryl ether (for example, vinyl phenyl ether, the vinyl tolyl ether, vinyl KURORU phenyl ether, vinyl -2, 4-dichloro phenyl ether, the vinyl naphthyl ether, the vinyl anthranil ether, etc.);

[0045] Vinyl ester, for example, vinyl butyrate, vinyl iso butyrate, Vinyl trimethyl acetate, vinyl diethyl acetate, vinyl BARETO, Vinyl caproate, vinyl KURORU acetate, vinyl dichloro acetate, Vinyl methoxy acetate, vinyl butoxy acetate, vinyl phenyl acetate, Vinyl acetoacetate, vinyl lactate, vinyl-beta-phenyl butyrate, vinyl cyclohexyl carboxylate, benzoic-acid vinyl, salicylic acid vinyl, Krol benzoic-acid vinyl, tetra-KURORU benzoic-acid vinyl, naphthoic-acid vinyl, etc.;

[0046] styrene, for example, styrene, and alkyl styrene (for example, methyl styrene --) Dimethyl styrene, trimethyl styrene, ethyl styrene, diethyl styrene, Isopropyl styrene, butyl styrene, hexyl styrene, cyclohexyl styrene, DESHIRU styrene, benzyl styrene, KURORU methyl styrene, trifluormethyl styrene, Alkoxy styrene, such as ethoxy methyl styrene and acetoxy methyl styrene for example, methoxy styrene and 4-methoxy-3-methyl styrene -- halogen styrene (for example, KURORU styrene --), such as dimethoxy styrene Dichloro styrene, TORIKURORU styrene, tetra-KURORU styrene, pen TAKURORU styrene, bromine styrene and a jib -- carboxy styrene [, such as ROM styrene, iodine styrene, Fluor styrene, Tori Fluor styrene, 2-bromine-4-trifluormethyl styrene, and 4-Fluor-3-trifluormethyl styrene,];

[0047] Crotonic-acid ester (for example, dimethyl itaconate, itaconic-acid diethyl, dibutyl itaconate, etc.), for example, crotonic-acid alkyl (for example, crotonic-acid butyl, crotonic-acid hexyl, glycerol mono-crotonate, etc.); itaconic-acid dialkyls,; there are the dialkyl ester of a maleic acid or boletic acid,

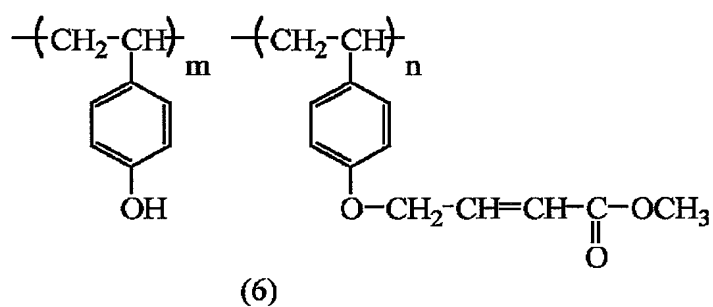
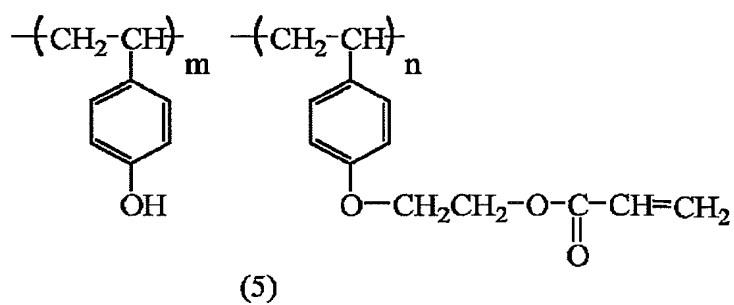
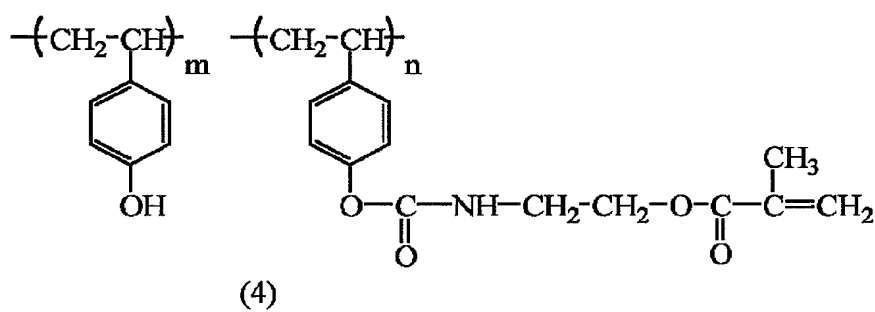
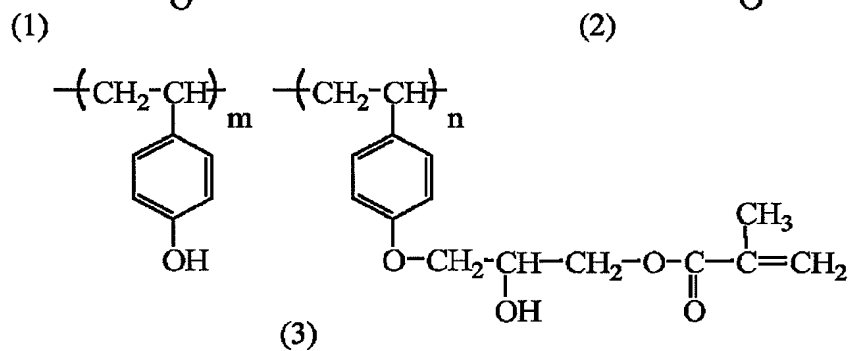
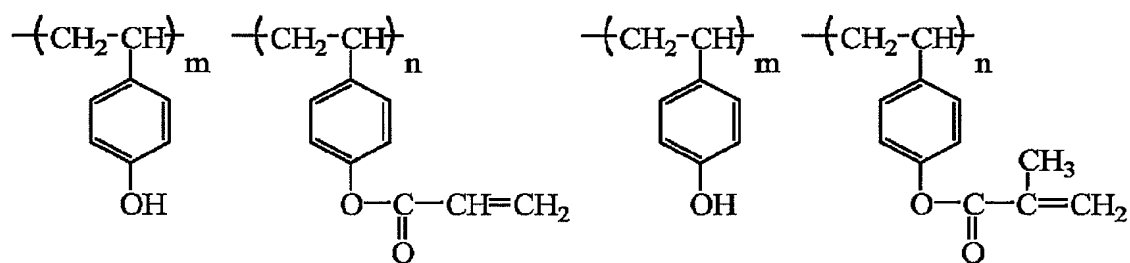
maleic anhydrides (for example, dimethyl MARERETO, dibutylfumarate, etc.), maleimide, acrylonitrile, a methacrylonitrile, MAREIRO nitril, etc. In addition, generally what is necessary is just a copolymerizable addition polymerization nature unsaturated compound.

[0048] In this, the monomer which has carboxyl groups, such as carboxy styrene, N-(carboxyphenyl) acrylamide, and N-(carboxyphenyl) methacrylamide, the maleimide of the monomer which raises alkali solubility, etc. are desirable as a copolymerization component. As a content of other polymerization nature monomers in the resin in this invention, less than [50 mol %] is desirable to all repeat units, and it is less than [30 mol %] more preferably.

[0049] Although the example of resin of having the repeat structural unit expressed with a general formula (a) below is shown, this invention is not limited to this.

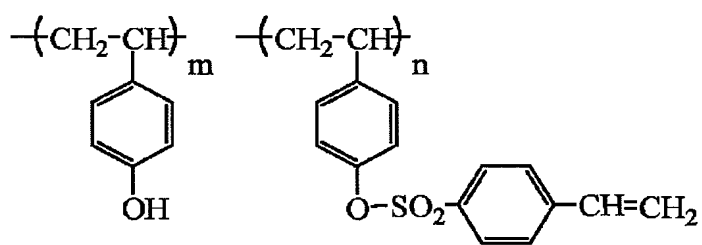
[0050]

[Formula 5]

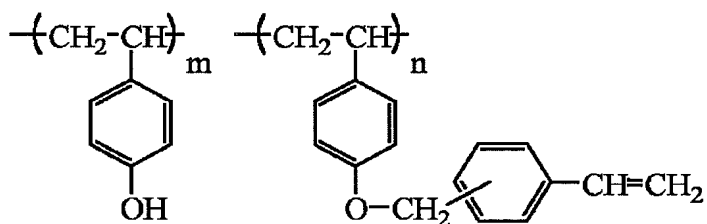


[0051]

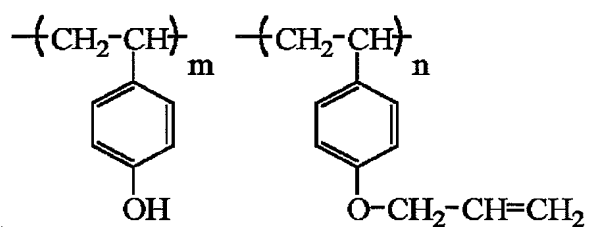
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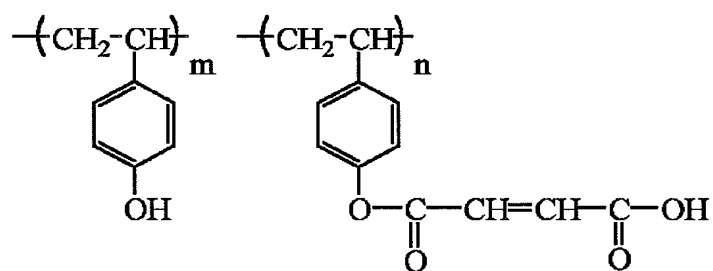
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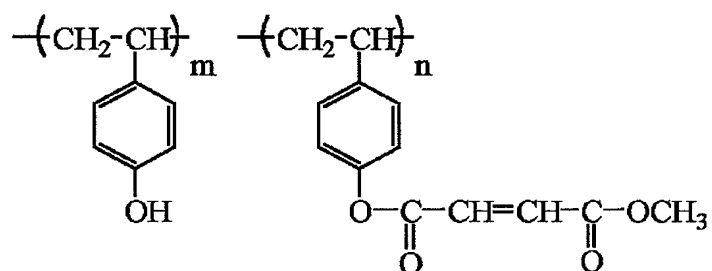
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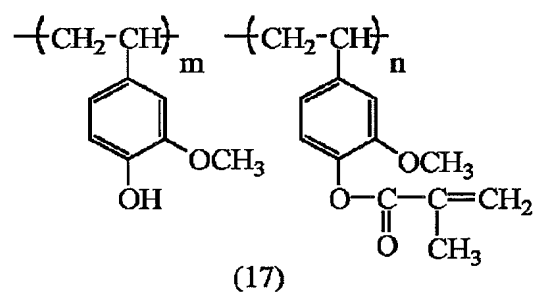
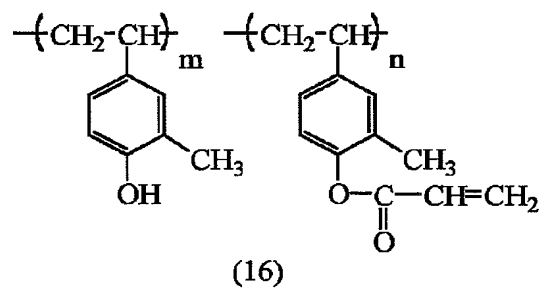
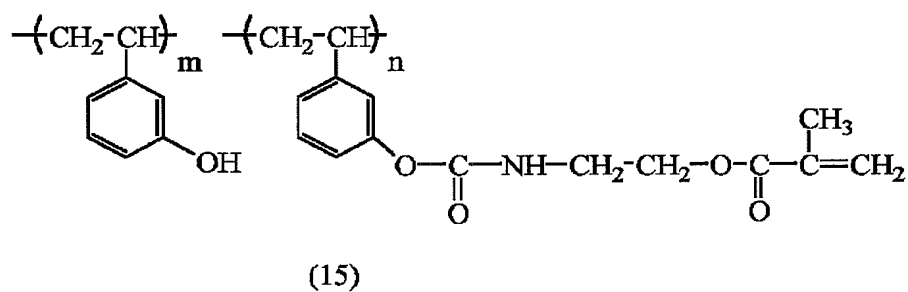
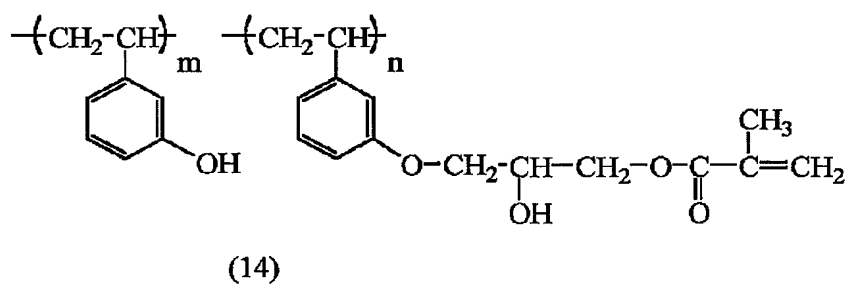
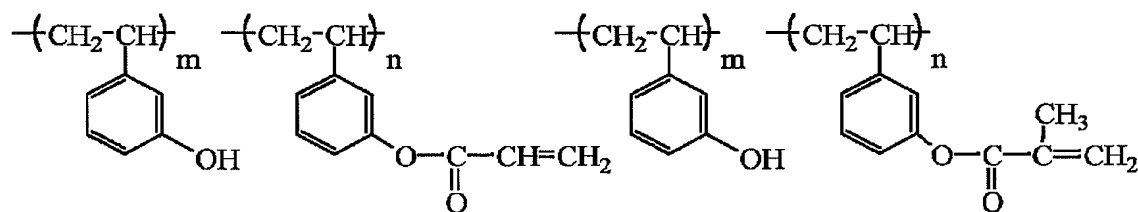
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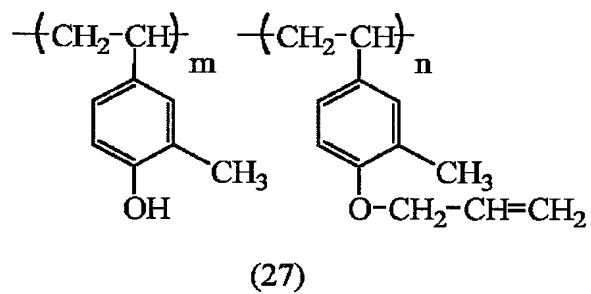
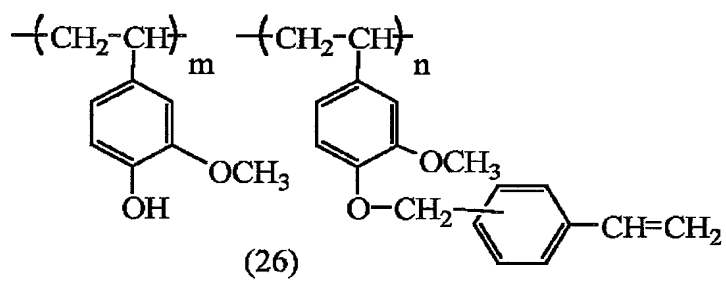
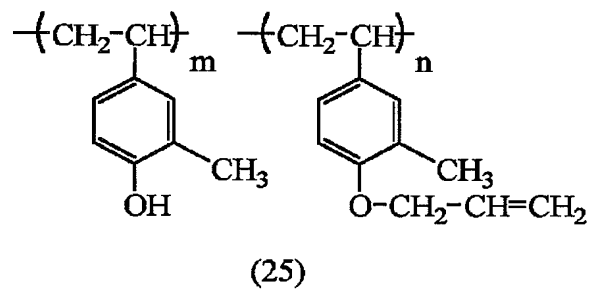
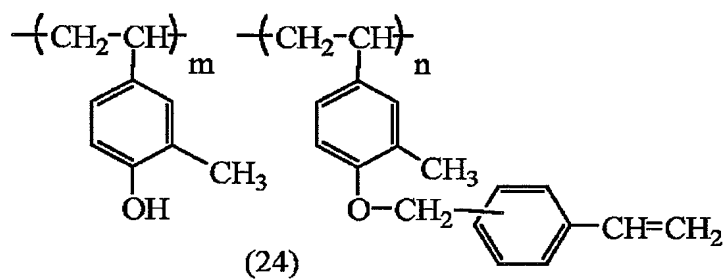
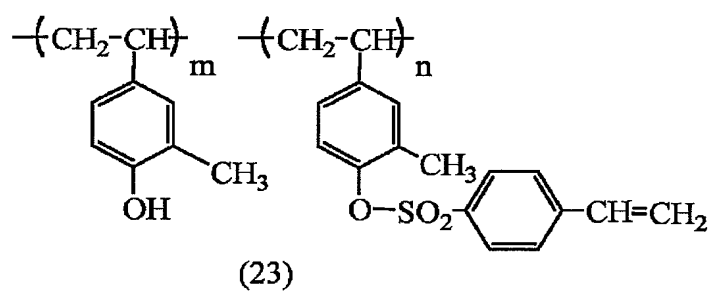
[0052]

[Formula 7]



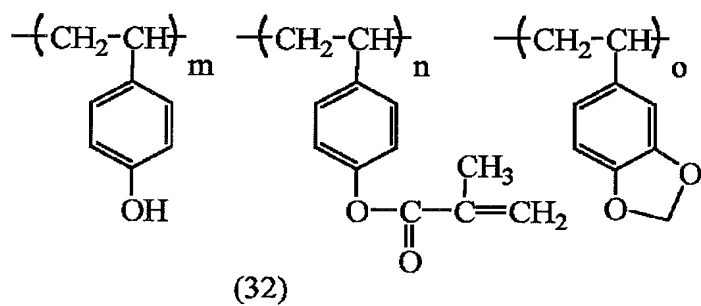
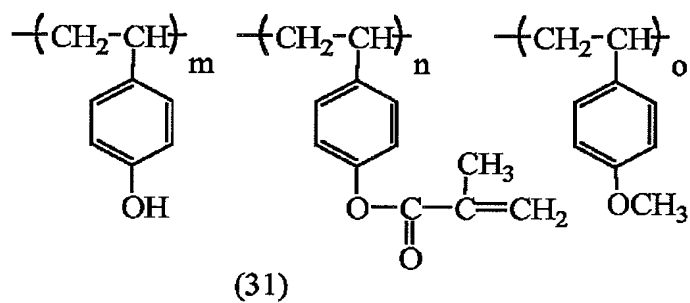
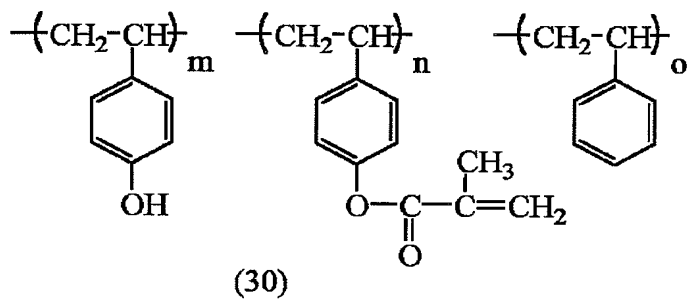
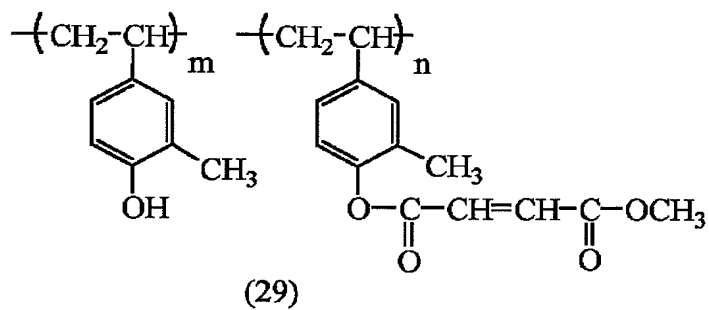
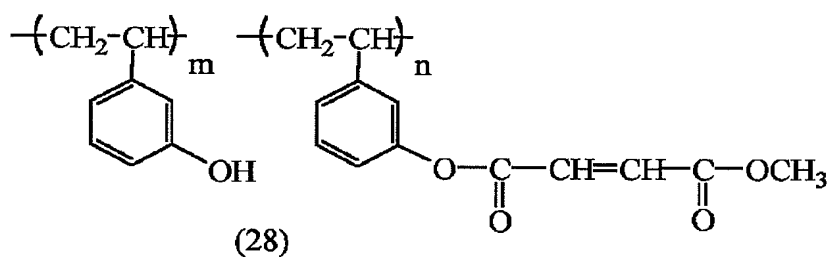
[0053]

[Formula 8]



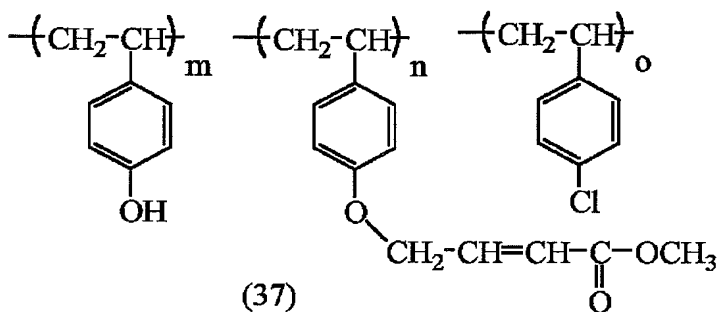
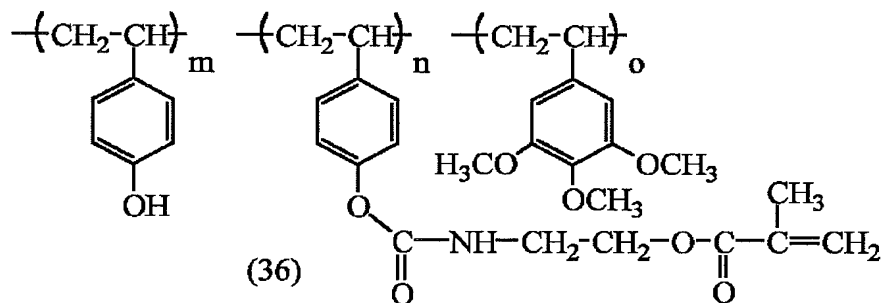
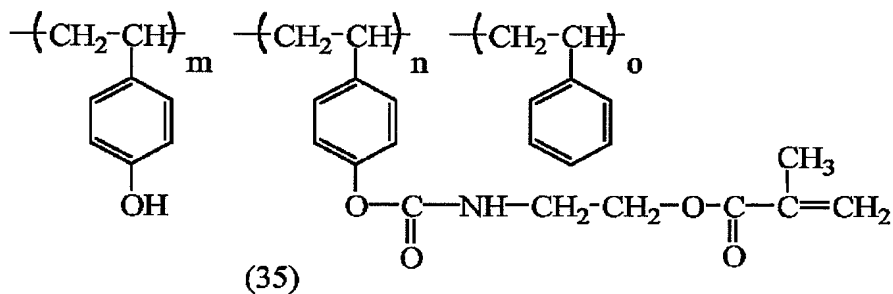
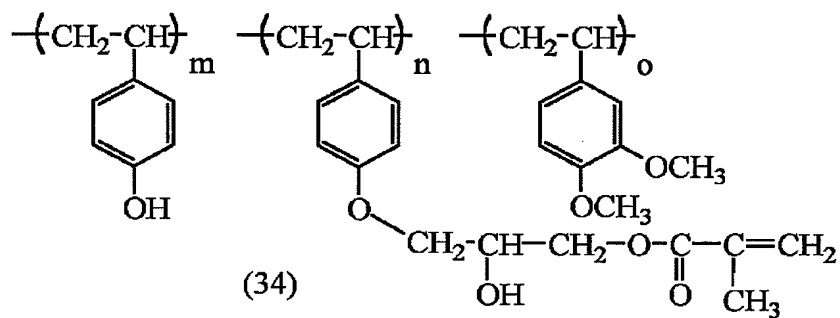
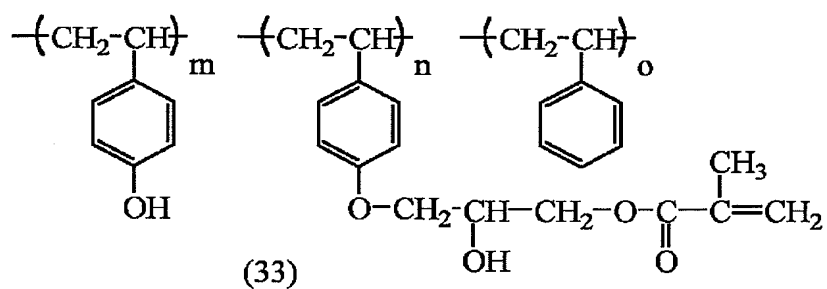
[0055]

[Formula 10]



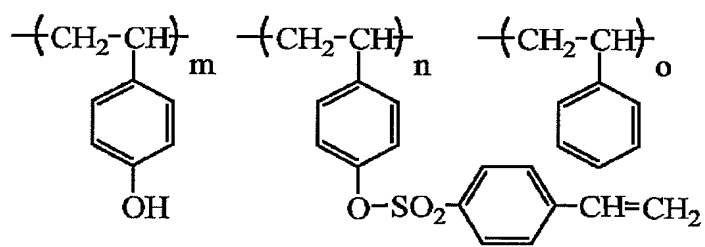
[0056]

[Formula 11]

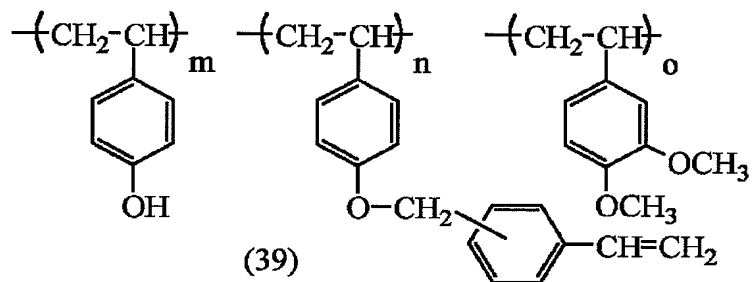


[0057]

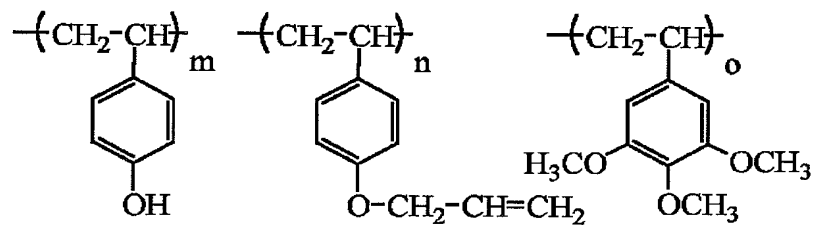
[Formula 12]



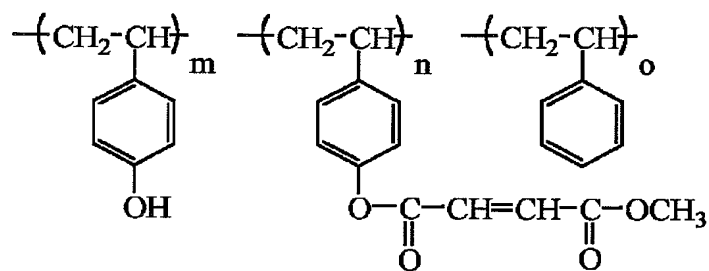
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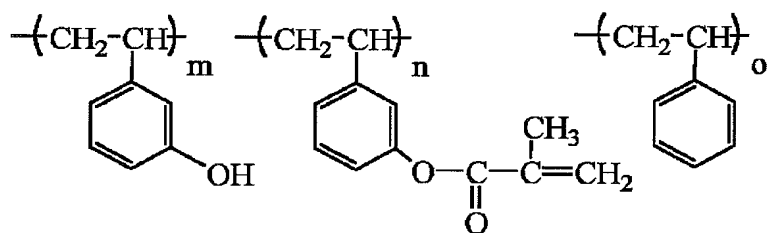
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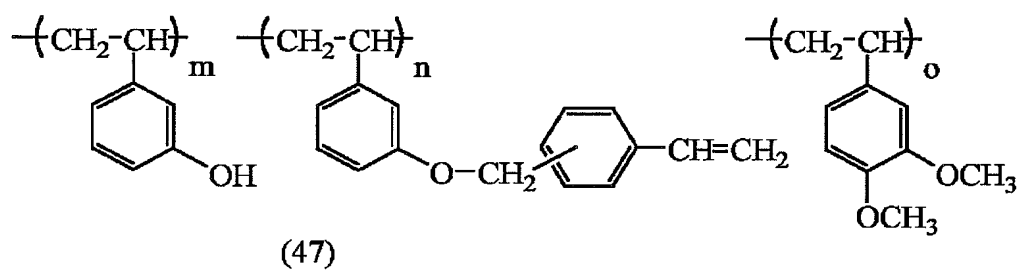
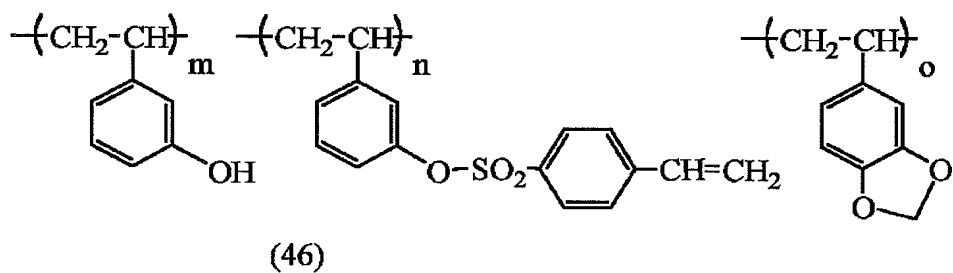
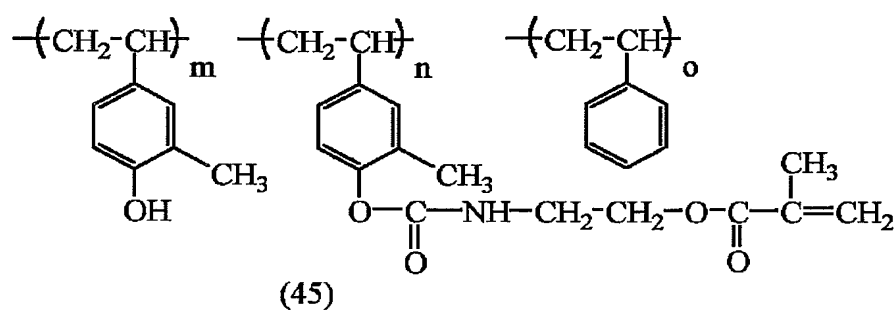
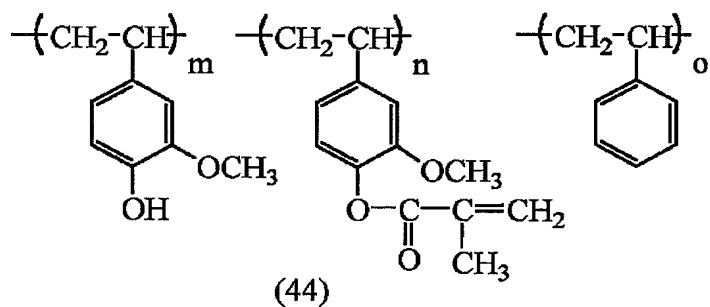
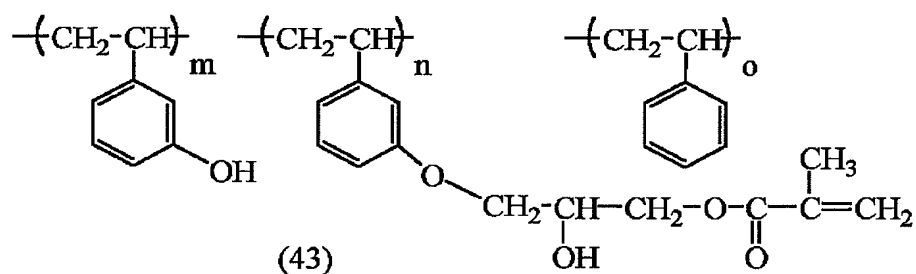
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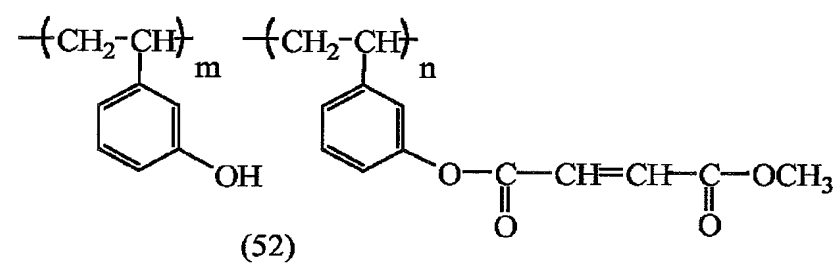
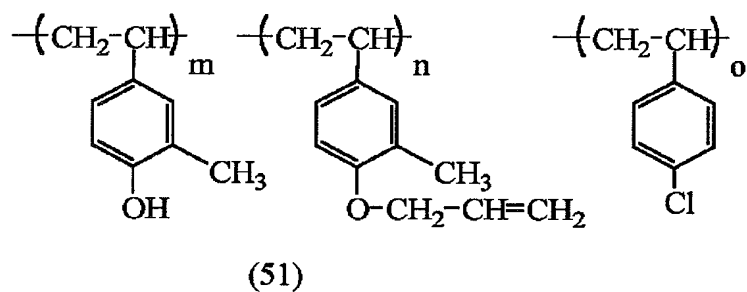
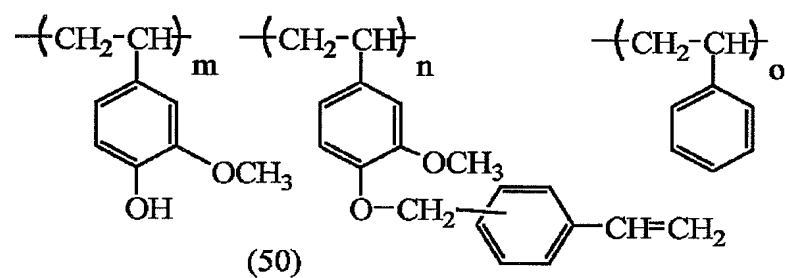
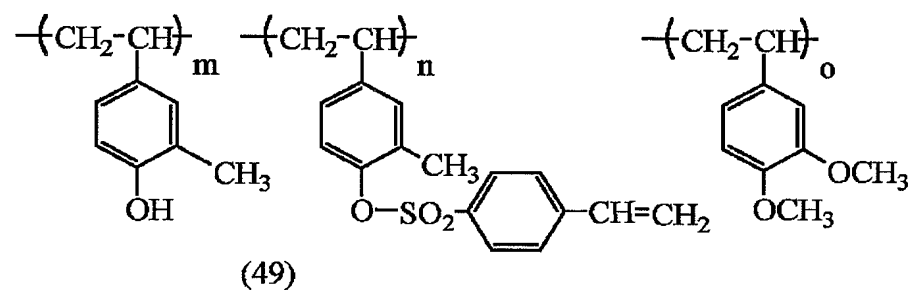
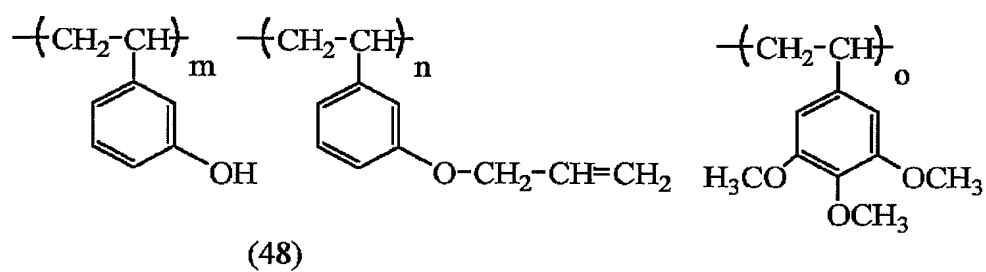
[0058]

[Formula 13]



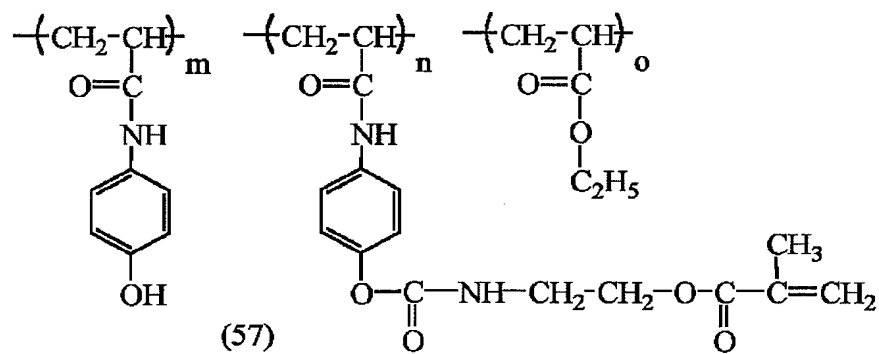
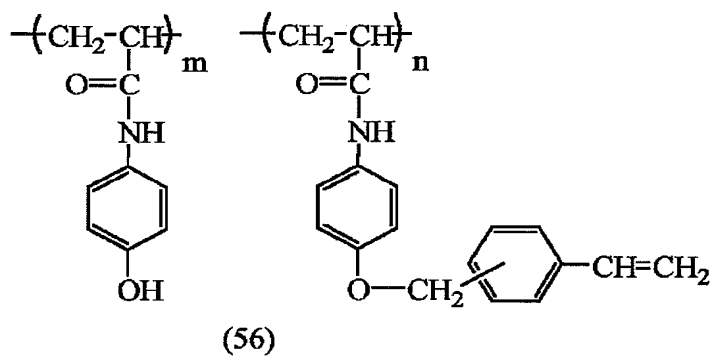
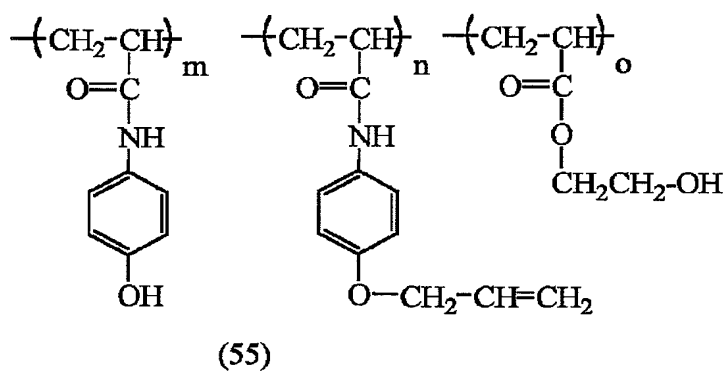
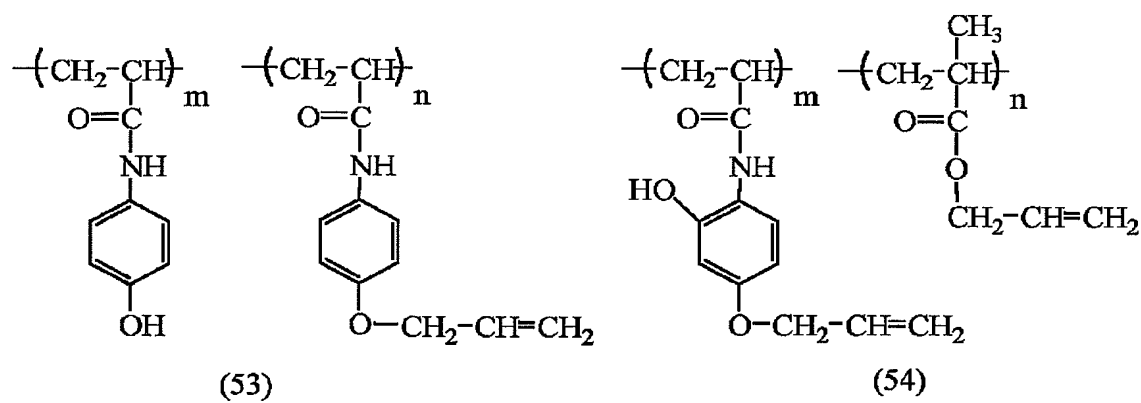
[0059]

[Formula 14]



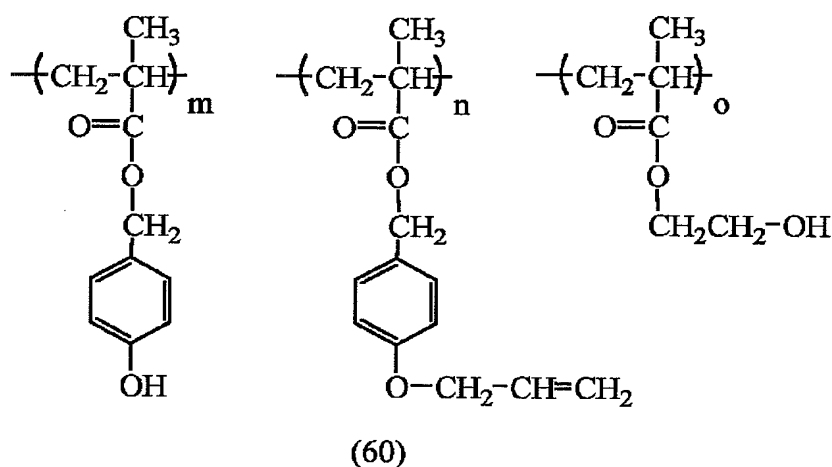
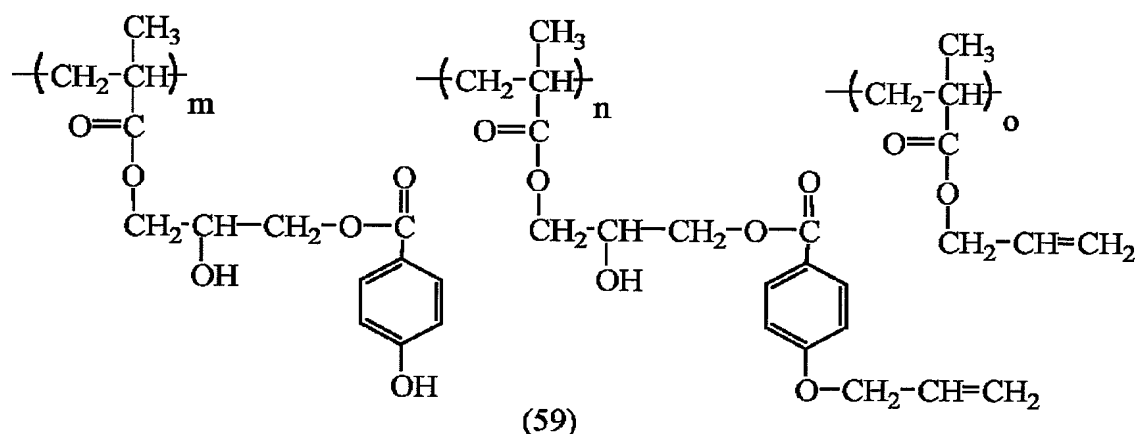
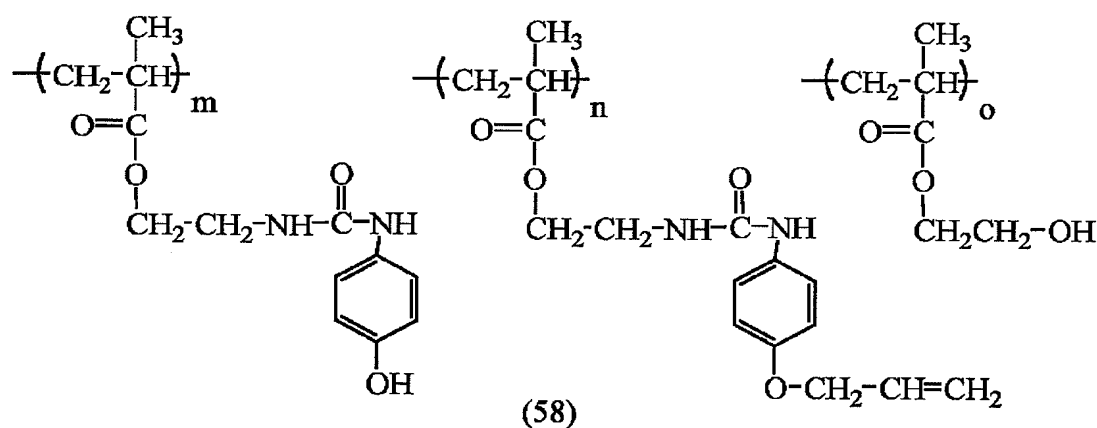
[0060]

[Formula 15]



[0061]

[Formula 16]



[0062] the resin which m, n, and o express the mole ratio of a resin presentation, and consists of two components -- m=10-95 and n=5-90 -- it is preferably used in m=40-90 and n=10-60. the resin which consists of three components -- m=10-90, n=5-85, and o=5-85 -- it is preferably used in m=40-80, n=10-50, and o=10-50.

[0063] The desirable molecular weight of the resin which has the above (B) and the repeat structural unit preferably expressed with a general formula (a) is 1,000-200,000 in a weighted mean, and is used in 3,000-50,000 still more preferably. molecular weight distribution -- 1-10 -- it is -- desirable -- 1-3 -- the

thing of the range of 1–1.5 is used still more preferably. What has a smaller molecular weight distribution has resolution, a resist configuration, and the more smooth side attachment wall of a resist pattern, and is excellent in roughness nature. the content of the repeat structural unit expressed with a general formula (a) — the whole resin — receiving — 5 – 100–mol % — it is 10 – 90–mol % preferably.

[0064] The alkali fusibility resin containing the structural unit expressed with the general formula (a) used for this invention is compoundable by the approach indicated by Macromolecules (1995), 28 (11), 3787–3789, Polym.Bull. (1990 (Berlin)), 24 (4), 385–389, and JP,8–286375,A. That is, target alkali fusibility resin can be obtained by the radical polymerization or the living anionic polymerization method. These resin may be used by one sort, and may mix and use plurality.

[0065] Here, weight average molecular weight has the polystyrene reduced property of gel permeation chromatography, and is defined. The alkali dissolution rate of alkali fusibility resin is measured by 0.261–N tetramethylammonium hydroxide (TMAH) (23 degrees C), and its thing 20A [/second] or more is desirable. It is a thing 200A [/second] or more especially preferably. Although the alkali fusibility resin of this invention may be used independently, it can also use other alkali fusibility resin together. The rate of an use rate can use together other alkali fusibility resin other than this invention to the a maximum of 100 weight section to the alkali fusibility resin 100 weight section of this invention. The alkali fusibility resin which can be used together below is illustrated.

[0066] For example, although novolak resin, hydrogenation novolak resin, acetone–pyrogallol resin, a styrene maleic anhydride copolymer, carboxyl group content methacrylic system resin, and its derivative can be mentioned, it is not limited to these. The addition of resin (B) is preferably used in 50 – 80% of the weight of the range still more preferably 40 to 90% of the weight 30 to 95% of the weight to the total solids of a constituent.

[0067] (2) Any compound can be used for it if the (A) component used for compound this invention which generates an acid and/or a radical kind by the exposure of the electron ray of this invention (A) or an X-ray is a compound which generates an acid and/or a radical kind by the exposure of an electron ray or an X-ray. Here, the compound which generates an acid and/or a radical kind expresses the compound which generates the compound or radical kind which generates the compound, acid, and radical kind which generate an acid.

[0068] By the exposure of such an electron ray or an X-ray, the compounds which generate an acid by the well-known light currently used for the photoinitiator of optical cationic polymerization, the photoinitiator of an optical radical polymerization, the optical decolorizing agent of coloring matter, optical alterant, or a micro resist, and those mixture can be used as a compound which generates an acid and/or a radical kind, choosing them suitably.

[0069] Moreover, the compound of a publication can be used for the radical which generates an acid and/or a radical kind or the compound which introduced the compound into the principal chain or side chain of a polymer, for example, JP,63–26653,A, JP,55–164824,A, JP,62–69263,A, JP,63–146038,A, JP,63–163452,A, JP,62–153853,A, JP,63–146029,A, etc. by the exposure of these electron rays or an X-ray. Furthermore, the compound which generates an acid by the light of a publication can also be used for U.S. Pat. No. 3,779,778, the Europe patent No. 126,712, etc.

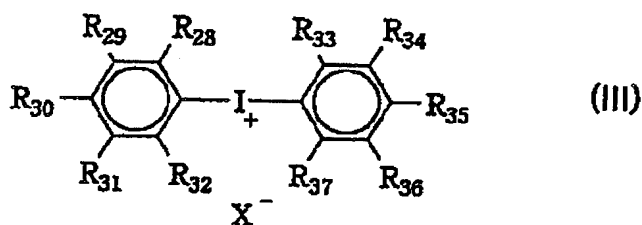
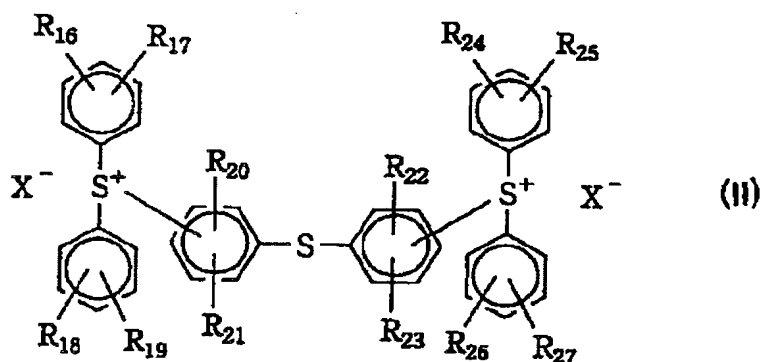
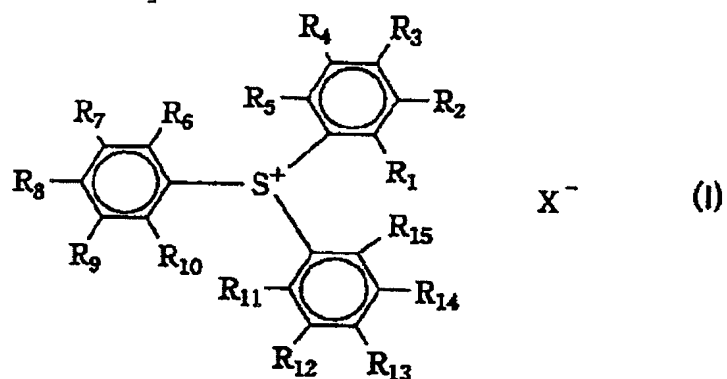
[0070] Moreover, onium salt, such as well-known diazonium salt, phosphonium salt, iodonium salt, sulfonium salt, and a seleno NIUMU salt, an organic halogenated compound, o-nitrobenzyl sulfonate compound, an

N-imino sulfonate compound, N-imide sulfonate compound, a diazo sulfone compound, a diazo disulfon compound, a disulfon compound, etc. can be mentioned.

[0071] Preferably, they are the sulfonate compound of sulfonium or iodonium, the sulfonate compound of N-hydroxy imide, or a disulfo nil diazomethane compound. Although the diazo disulfon compound of a publication, the sulfonium salt further expressed with the following general formula (I) - (III), and iodonium salt can be mentioned to N-imide sulfonate compound given in JP,10-7653,A, JP,11-2901,A, etc., JP,4-210960,A, the Europe patent No. 417557, etc. especially preferably in these, the sulfonium salt and iodonium salt which are expressed with the following general formula (I) - (III) are the most desirable.

[0072]

[Formula 17]



[0073] R1-R37 in a general formula (I) - a general formula (III) are a hydrogen atom, an alkyl group, an alkoxy group, hydroxyl, a halogen atom, or the radical that can be shown by -S-R38. A straight chain-like is sufficient as the alkyl group which R1-R37 express, the letter of branching is sufficient as it, and annular is sufficient as it. As the shape of a straight chain, and a letter alkyl group of branching, the alkyl group of 1-4 carbon numbers, such as a methyl group, an ethyl group, a propyl group, n-butyl, sec-butyl, and t-butyl, can

be mentioned, for example. As an annular alkyl group, alkyl groups of 3–8 carbon numbers, such as a cyclopropyl group, a cyclopentyl group, and a cyclohexyl radical, can be mentioned, for example.

[0074] A straight chain-like is sufficient as the alkoxy group which R1–R37 express, the letter of branching is sufficient as it, and an annular alkoxy group is sufficient as it. As the shape of a straight chain, and a letter alkoxy group of branching, the thing of 1–8 carbon numbers, for example, a methoxy group, an ethoxy radical, a hydroxy ethoxy radical, a propoxy group, an n-butoxy radical, an iso butoxy radical, a sec-butoxy radical, a t-butoxy radical, an octyloxy radical, etc. can be mentioned, for example. As an annular alkoxy group, a cyclopenthyloxy radical and a cyclohexyloxy radical are mentioned, for example.

[0075] As an annular alkoxy group, a cyclopenthyloxy radical and a cyclohexyloxy radical are mentioned, for example. As a halogen atom which R1–R37 express, a fluorine atom, a chlorine atom, a bromine atom, and iodine atom can be mentioned. R38 in –S–R38 which R1–R37 express is an alkyl group or an aryl group. All in the alkyl group already enumerated as range of the alkyl group which R38 expresses as an alkyl group which R1–R37 express, for example can be mentioned. The aryl group which R38 expresses can mention the aryl group of 6–14 carbon numbers, such as a phenyl group, a tolyl group, a methoxyphenyl radical, and a naphthyl group.

[0076] Each of alkyl groups which the alkyl group and alkoxy group which R1–R37 express, or R38 expresses, and aryl groups could combine the substituent with a part of radical further, may increase the carbon number, and does not need to have the substituent. Furthermore, as a substituent which may be combined, the alkoxy group of 1–4 carbon numbers, the aryl group of 6–10 carbon numbers, and the alkenyl radical of 2–6 carbon numbers can be mentioned, and a cyano group, hydroxyl, a carboxy group, an alkoxy carbonyl group, a nitro group, etc. can be mentioned preferably. In addition, a halogen atom is sufficient. For example, a fluorine atom, a chlorine atom, and iodine atom can be mentioned.

[0077] Two or more of them may join together, and the radical shown by R1–R15 in a general formula (I) may form the ring. The end of the radical shown by R1–R15 may couple directly and form a ring. Through one sort or two sorts or more of elements chosen from carbon, oxygen, sulfur, and nitrogen, it may connect indirectly, and may suit, and the ring may be formed. The structure same as a ring structure which two or more of R1–R15 combine and form as the ring structure looked at by a furan ring, a dihydrofuran ring, a pyran ring, a trihydro pyran ring, a thiophene ring, the pyrrole ring, etc. can be mentioned. It can say that the same is said of R16–R27 in a general formula (II). Two or more may join together directly or indirectly, and they may form the ring. The same is said of R28–R37 in a general formula (III).

[0078] A general formula (I) – (III) have X⁻. X⁻ which a general formula (I) – (III) have is the anion of an acid. The acid which forms the anion is an acid chosen from benzenesulfonic acid, a naphthalene sulfonic acid, or an anthracene sulfonic acid. One or more fluorine atoms have permuted by the acid. or the acid -- the fluorine atom -- or a fluorine atom -- replacing with -- an alkyl group, an alkoxyl group, an acyl group, an acyloxyl radical, a sulfonyl group, a sulfonyloxy radical, a sulfonylamino radical, an aryl group, an aralkyl radical, and an alkoxy carbonyl group -- since -- having at least one sort of organic radicals chosen from the becoming group, moreover, the organic radical has permuted at least one fluorine atom further. Moreover, benzenesulfonic acid, an above-mentioned naphthalene sulfonic acid, or an above-mentioned anthracene sulfonic acid may be permuted by halogen atoms other than a fluorine, the hydroxyl group, the nitro group, etc.

[0079] The alkyl group combined with the benzenesulfonic acid which forms the anion of X⁻ is an alkyl group of carbon numbers 1–12. A straight chain-like is sufficient as an alkyl group, the letter of branching is sufficient as it, and annular is sufficient as it. at least one fluorine atom — 25 or less fluorine atoms have permuted preferably. Specifically, a TORIFURORO methyl group, the Pentough Rollo ethyl group, 2 and 2, 2-TORIFURORO ethyl group, a heptaphloropropyl radical, a hepta-FURORO isopropyl group, perphloro butyl, a perphloro octyl radical, the perphloro dodecyl, a perphloro cyclohexyl radical, etc. can be mentioned. Especially, the perphloroalkyl group of the carbon numbers 1–4 altogether permuted with the fluorine is desirable.

[0080] an alkyl group — or the carbon number of the alkoxy group independently combined with the above-mentioned benzenesulfonic acid etc. is the alkoxy group of 1–12. A straight chain-like is sufficient as an alkoxy group, the letter of branching is sufficient as it, and annular is sufficient as it. at least one fluorine atom — 25 or less fluorine atoms have permuted preferably. Specifically, a TORIFURORO methoxy group, a pen TAFURORO ethoxy radical, a hepta-FURORO isopropoxy radical, a perphloro butoxy radical, a perphloro octyloxy radical, a perphloro dodecyloxy radical, a perphloro cyclohexyloxy radical, etc. can be mentioned. Especially, the perphloro alkoxy group of the carbon numbers 1–4 altogether permuted with the fluorine is desirable.

[0081] an alkyl group — or as for the acyl group independently combined with the above-mentioned benzenesulfonic acid etc., what is permuted by carbon numbers 2–12 and 1–23 fluorine atoms is desirable. Specifically, the Tori Flo Roar cetyl group, the Flo Roar cetyl group, a pen TAFURORO propionyl radical, the Pentough Rollo benzoyl, etc. can be mentioned.

[0082] an alkyl group — or the acyloxy radical independently combined with the above-mentioned benzenesulfonic acid etc. has that desirable by which the carbon number is permuted by the fluorine atom they are [atom] 2–12, and 1–23 pieces. Specifically, a TORIFURORO acetoxy radical, a FURORO acetoxy radical, a pen TAFURORO propionyloxy radical, a pen TAFURORO benzoyloxy radical, etc. can be mentioned. an alkyl group — or that by which the carbon number is permuted as a sulfonyl group independently combined with the above-mentioned benzenesulfonic acid etc. by the fluorine atom they are [atom] 1–12, and 1–25 pieces is desirable. Specifically, a truffe ROROME tongue sulfonyl group, the Pentough ROROE tongue sulfonyl group, a perphloro butane sulfonyl group, a perphloro octane sulfonyl group, a pen TAFURORO benzenesulphonyl radical, 4-trifluoromethylbenzene sulfonyl group, etc. can be mentioned.

[0083] an alkyl group — or that by which the carbon number is permuted by the fluorine atom they are [atom] 1–12, and 1–25 pieces as the above-mentioned sulfonyloxy radical independently combined with the above-mentioned benzenesulfonic acid etc. is desirable. Specifically, truffe ROROME tongue sulfonyloxy, a perphloro butane sulfonyloxy radical, 4-trifluoromethylbenzene sulfonyloxy radical, etc. can be mentioned. an alkyl group — or as the above-mentioned sulfonylamino radical independently combined with the above-mentioned benzenesulfonic acid etc., carbon numbers are 1–12 and what is permuted by 1–25 fluorine atoms is desirable. Specifically, a truffe ROROME tongue sulfonylamino radical, a perphloro butane sulfonylamino radical, a perphloro octane sulfonylamino radical, a pen TAFURORO benzenesulphonyl amino radical, etc. can be mentioned.

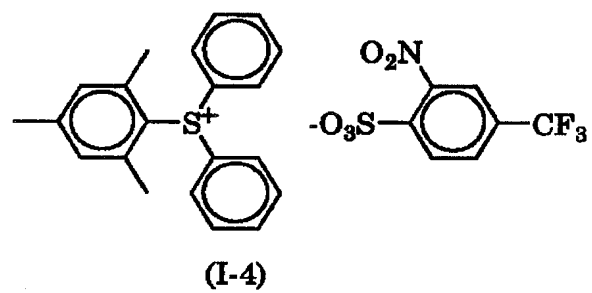
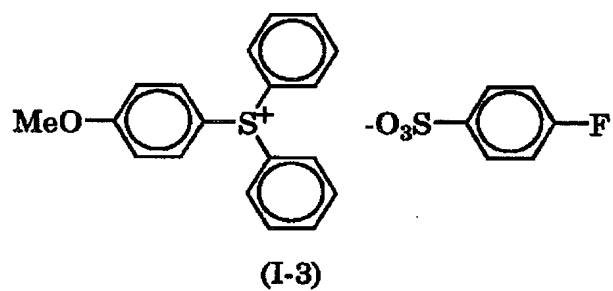
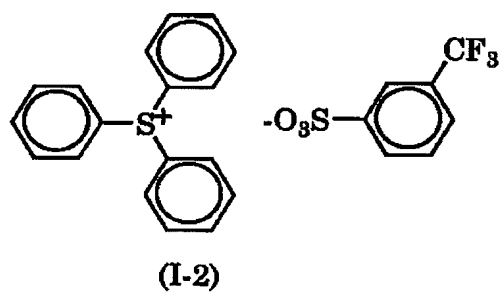
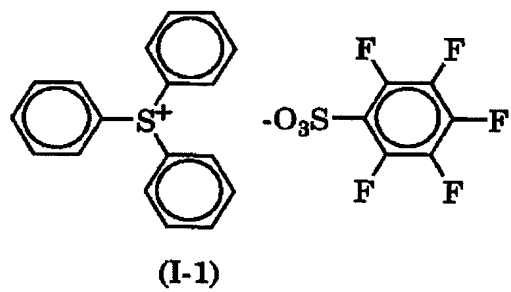
[0084] an alkyl group — or that by which the carbon number is permuted by the fluorine atom they are [atom] 6–14, and 1–9 pieces as the above-mentioned aryl group independently combined with the

above-mentioned benzenesulfonic acid etc. is desirable. Specifically, Pentough Rollo phenyl group, 4-truffe ROROME chill phenyl group, hepta-FURORO naphthyl group, nona FURORO anthranil, 4-FURORO phenyl group, 2, and 4-JIFURORO phenyl group etc. can be mentioned. an alkyl group -- or that by which the carbon number is permuted by the fluorine atom they are [atom] 7-10, and 1-15 pieces as the above-mentioned aralkyl radical independently combined with the above-mentioned benzenesulfonic acid etc. is desirable. Specifically, a pen TAFURORO phenylmethyl radical, a pen TAFURORO phenylethyl radical, perphloro benzyl, a perphloro phenethyl radical, etc. can be mentioned. an alkyl group -- or that by which the carbon number is permuted by the fluorine atom they are [atom] 2-13, and 1-25 pieces as the above-mentioned alkoxy carbonyl group independently combined with the above-mentioned benzenesulfonic acid etc. is desirable. Specifically, a TORIFURORO methoxycarbonyl group, a pen TAFURORO ethoxycarbonyl radical, a pen TAFURORO phenoxy carbonyl group, a perphloro butoxycarbonyl radical, a perphloro octyloxy carbonyl group, etc. can be mentioned.

[0085] Most desirable X- in such an anion is a fluorine permutation benzenesulfonic acid anion, and especially its pentafluoro benzenesulfonic acid anion is desirable especially. Moreover, the benzenesulfonic acid which has the above-mentioned fluorine-containing substituent, a naphthalene sulfonic acid, or an anthracene sulfonic acid may be further permuted by the shape of a straight chain, the letter of branching or an annular alkoxy group, an acyl group, an acyloxy radical, a sulfonyl group, a sulfonyloxy radical, a sulfonylamino radical, an aryl group, an aralkyl radical, the alkoxy carbonyl group (these carbon number range is the same as that of the aforementioned thing), the halogen (except for a fluorine), the hydroxyl group, a nitro group, etc. Although the example of a compound expressed with these general formulas (I) - (III) below is shown, it is not limited to this.

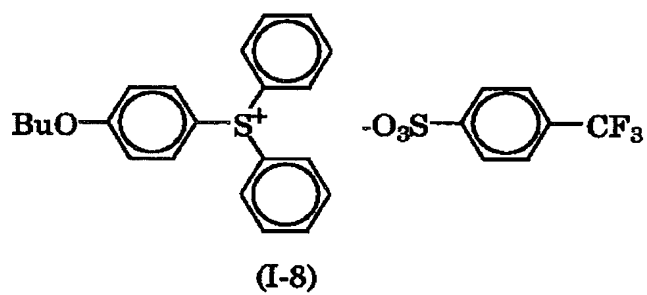
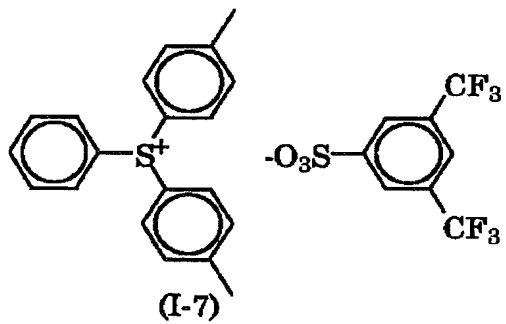
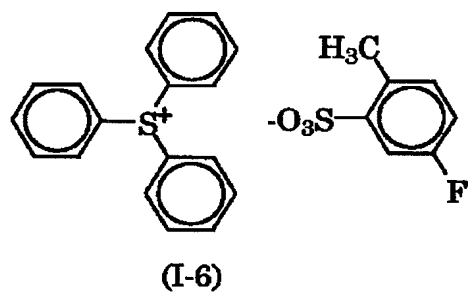
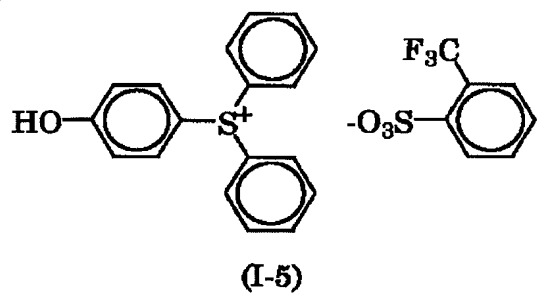
[0086]

[Formula 18]



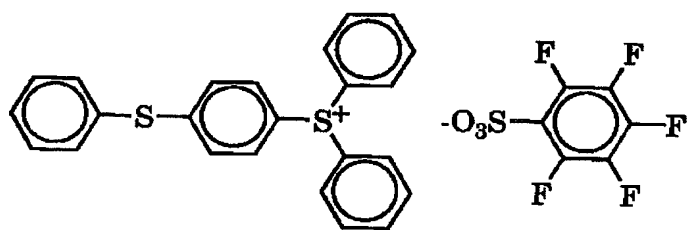
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[Formula 19]

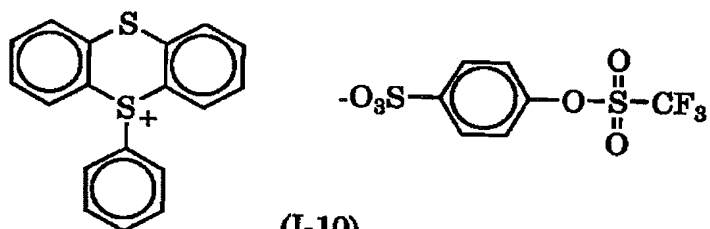


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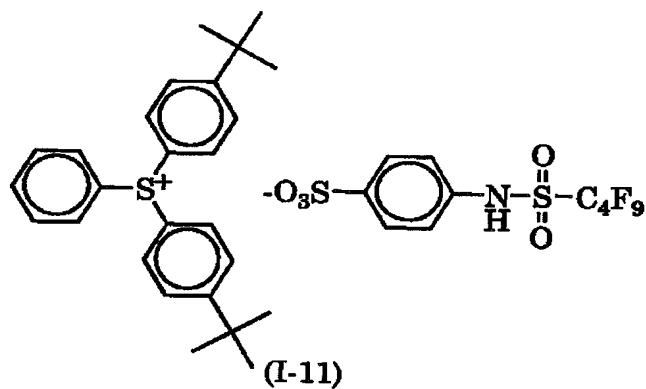
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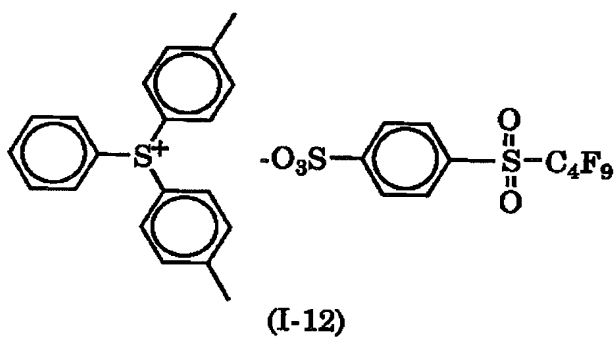
(I-9)



(I-10)



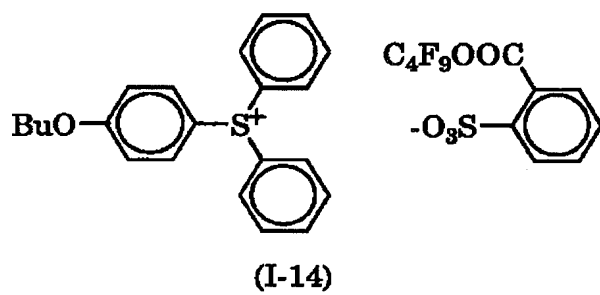
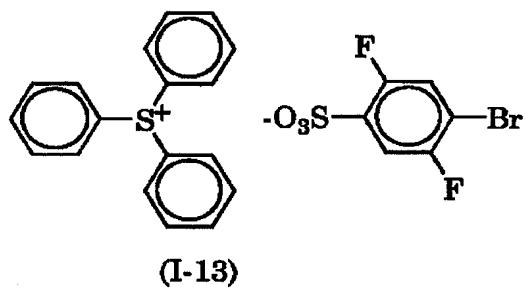
(I-11)



(I-12)

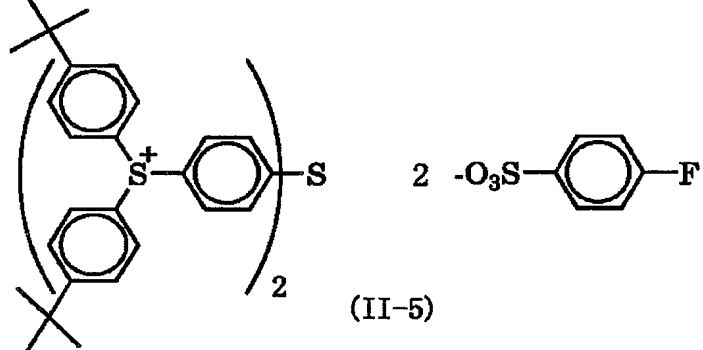
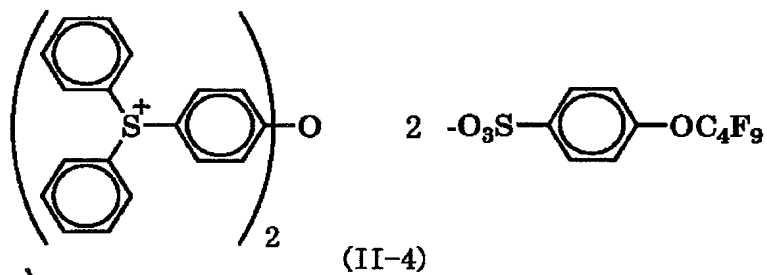
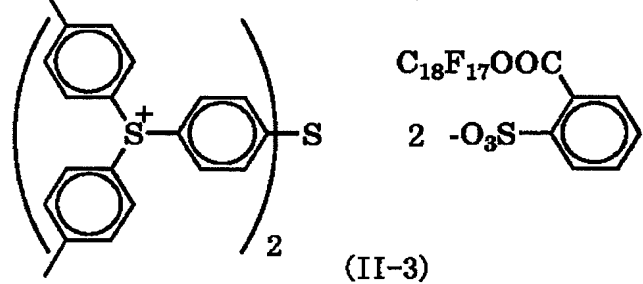
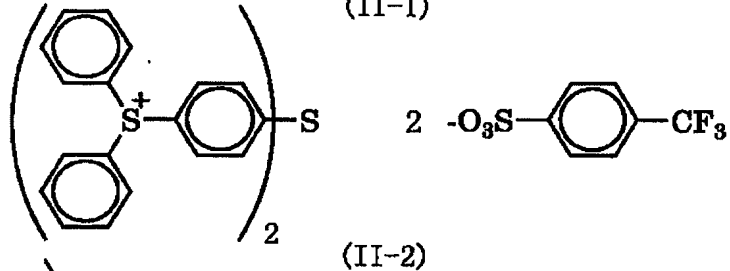
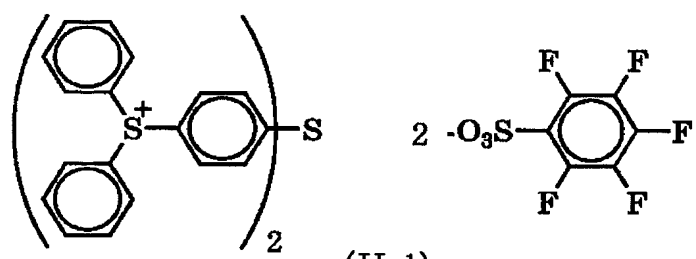
[0089]

[Formula 21]



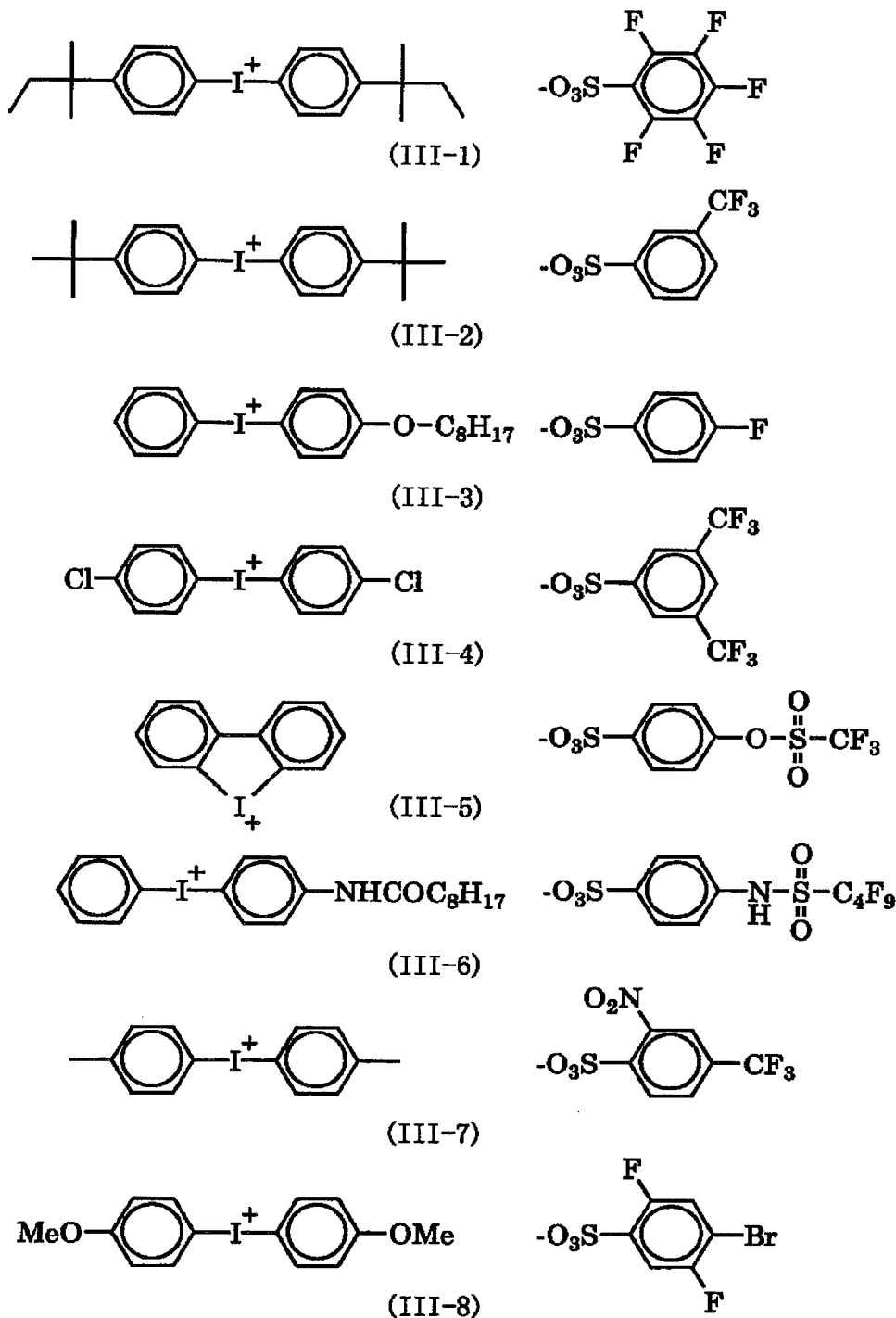
[0090]

[Formula 22]



[0091]

[Formula 23]



[0092] The compound of a general formula (I) and a general formula (II) is compoundable by the following approaches. For example, an aryl Grignard reagent and phenyl sulfoxides, such as aryl magnesium bromide, are made to react, and salt exchange of the obtained triarylsulfonium halide is carried out with a corresponding sulfonic acid. There is also an option. For example, there are condensation and the approach of carrying out salt exchange using acid catalysts, such as methansulfonic acid / diphosphorus pentoxide, or chlorination aluminum, about a phenyl sulfoxide and a corresponding aromatic compound. Moreover, a diaryl iodonium salt and a diaryl sulfide are compoundable by condensation, the approach of carrying out salt

exchange, etc. using catalysts, such as copper acetate. The phenyl sulfoxide may be making the substituent permute by the benzene ring by any above-mentioned approach, and there may not be such a substituent. The compound of a general formula (III) is compoundable by making an aromatic compound react using a periodate.

[0093] 0.1 – 20 % of the weight is suitable for the content of the (A) component used by this invention to the solid content of all negative-resist constituents, and it is 1 – 7 % of the weight still more preferably 0.5 to 10% of the weight preferably.

[0094] In this invention, other compounds which decompose by the exposure of a radiation and generate an acid and/or a radical kind with these in addition to the compound expressed with the above-mentioned general formula (I) – a general formula (III) can be used. the ratio of other compounds which decompose by the exposure of a radiation and generate an acid and/or a radical kind in using other compounds which decompose by the exposure of a radiation and generate an acid and/or a radical kind with the compound expressed with a general formula (I) – a general formula (III) -- a mole ratio -- 100 / 0 – 20/80 -- desirable -- 90 / 10 – 40/60 -- it is 80 / 20 – 50/50 still more preferably.

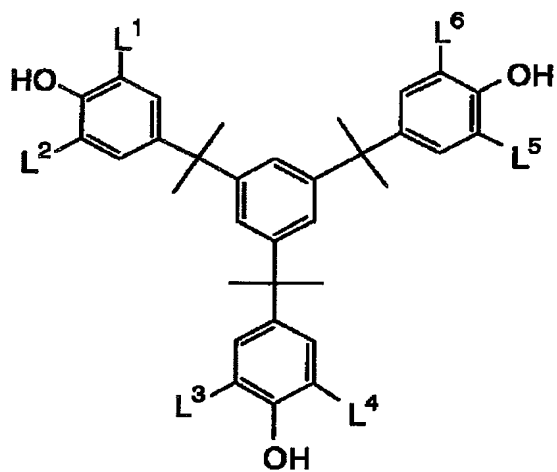
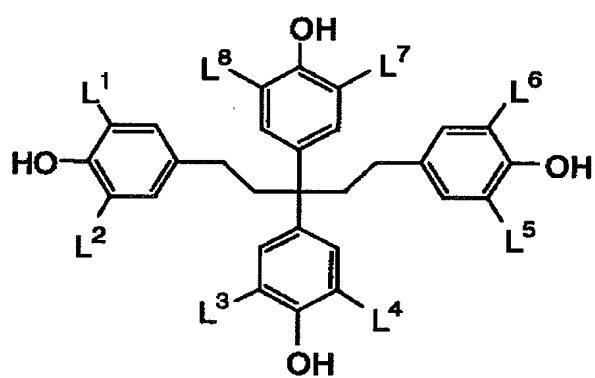
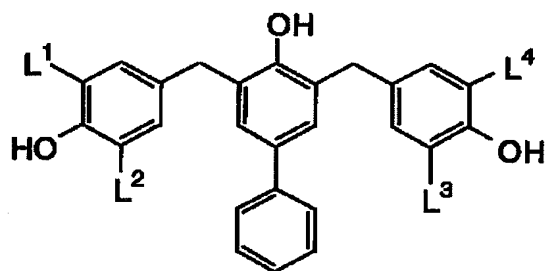
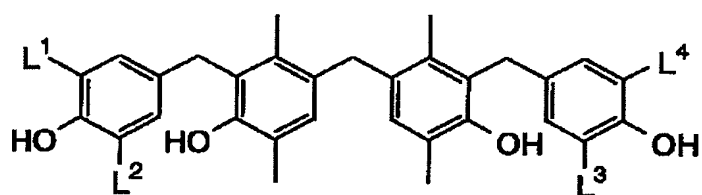
[0095] (3) use the compound (the following -- suitably -- an acid cross linking agent -- or a cross linking agent is only called) which constructs a bridge with an acid with alkali fusibility resin, an acid, and/or a radical generating agent in acid cross linking agent this invention of this invention (C). Here, a well-known acid cross linking agent can be used effectively. Preferably, they are the compound which has a hydroxymethyl group, an alkoxy methyl group, an acyloxy methyl group, or two or more alkoxy methyl ether radicals, resin, or an epoxy compound.

[0096] Furthermore, an alkoxy methylation, acyloxy methylation melamine compound or resin, alkoxy methylation, acyloxy methylation urea compound or resin, hydroxymethyl-izing, alkoxy methylation phenolic compound or resin, and alkoxy methyl ether-ized phenolic compound or resin is mentioned preferably.

[0097] Specifically, a cross linking agent can use a phenol derivative. Preferably, molecular weight has a hydroxymethyl group or two or more alkoxy methyl groups in all further including the 3–5 benzene rings in 1200 or less and intramolecular, and the hydroxymethyl group and an alkoxy methyl group can be centralized on one of the benzene rings at least, or the phenol derivative which it distributes and comes to join together can be mentioned. By using such a phenol derivative, effectiveness of this invention can be made more remarkable. As an alkoxy methyl group combined with the benzene ring, the thing of six or less carbon numbers is desirable. Specifically, a methoxymethyl radical, an ethoxy methyl group, an n-propoxy methyl group, an i-propoxy methyl group, an n-butoxy methyl group, an i-butoxy methyl group, a sec-butoxy methyl group, and a t-butoxy methyl group are desirable. Furthermore, the alkoxy group by which the alkoxy permutation was carried out is also desirable like a 2-methoxyethoxy radical and a 2-methoxy-1-propyl group. A desirable thing is especially listed to below among these phenol derivatives.

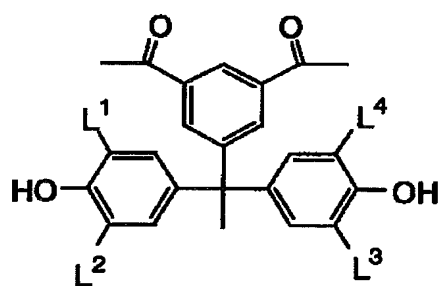
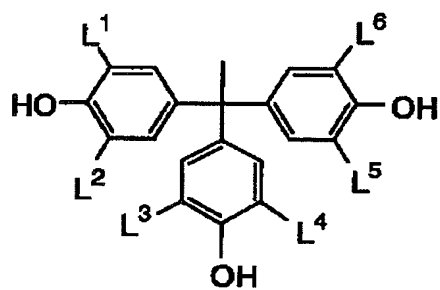
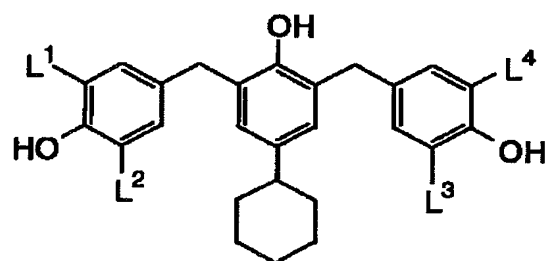
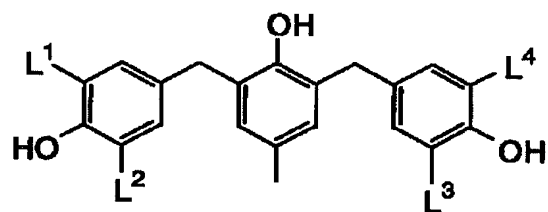
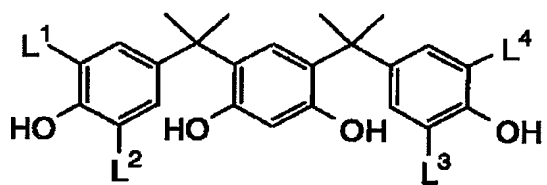
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[Formula 24]



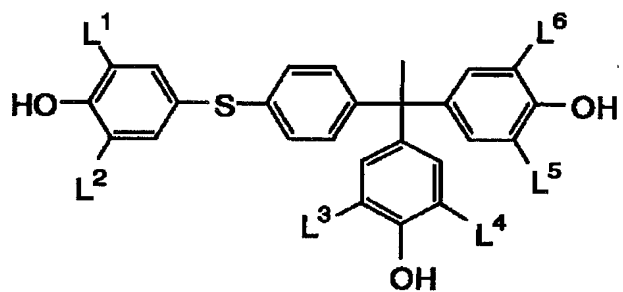
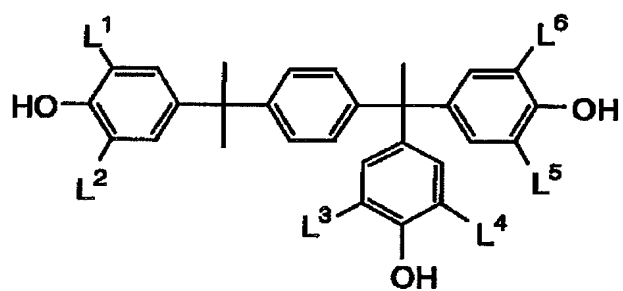
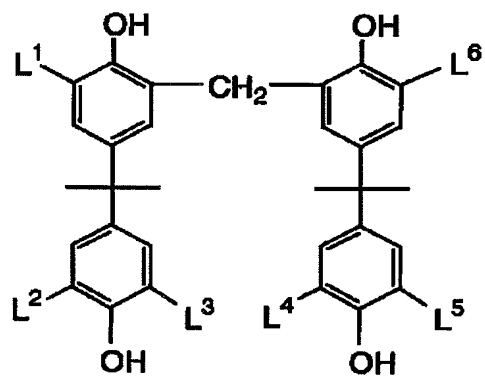
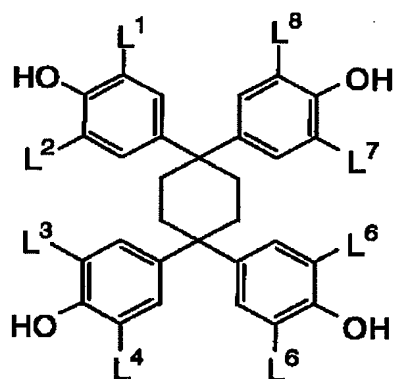
[0099]

[Formula 25]



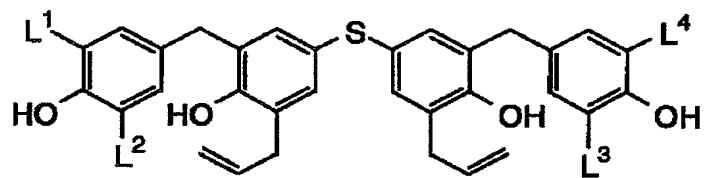
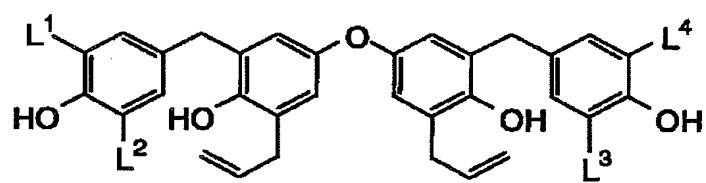
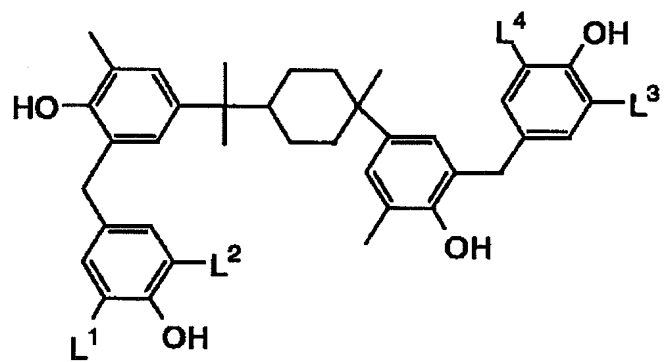
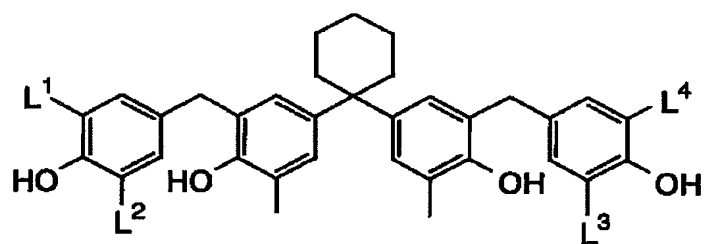
[0100]

[Formula 26]



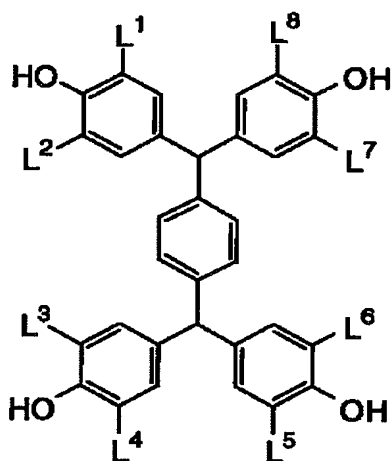
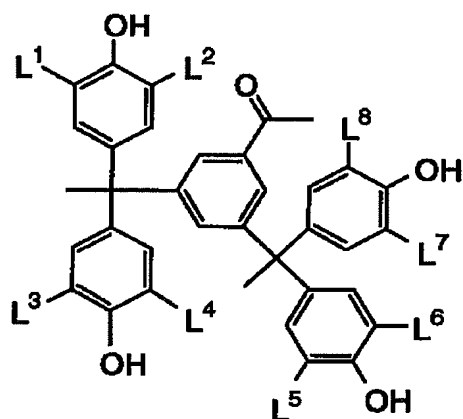
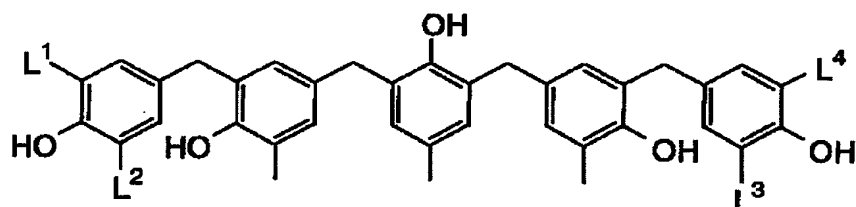
[0101]

[Formula 27]



[0102]

[Formula 28]



[0103] (Among a formula, even if L1-L8 are the same, they may differ from each other, and they show a hydroxymethyl group, a methoxymethyl radical, or an ethoxy methyl group.)

The phenol derivative which has a hydroxymethyl group can be obtained by making the phenolic compound (compound L1-whose L8 are the hydrogen atoms in the above-mentioned formula) and formaldehyde which do not have a corresponding hydroxymethyl group react under a base catalyst. Under the present circumstances, in order to prevent resinification and gelation, it is desirable to perform reaction temperature below 60 degrees C. Specifically, it is compoundable by the approach indicated by JP,6-282067,A, JP,7-64285,A, etc.

[0104] The phenol derivative which has an alkoxy methyl group can be obtained by making the phenol derivative and alcohol which have a corresponding hydroxymethyl group react under an acid catalyst. Under the present circumstances, in order to prevent resinification and gelation, it is desirable to perform reaction temperature below 100 degrees C. Specifically, it is compoundable by the approach indicated by the Europe

patent EP632003A1 grade. Thus, although the phenol derivative which has the compounded hydroxymethyl group or alkoxy methyl group is desirable in respect of the stability at the time of preservation, especially the phenol derivative that has an alkoxy methyl group is desirable from a viewpoint of the stability at the time of preservation. Such a phenol derivative that has a hydroxymethyl group or two or more alkoxy methyl groups in all, and is made to concentrate on one of the benzene rings, or distributes, and it comes to join together may be used independently, and may be used combining two or more sorts.

[0105] Besides the above-mentioned phenol derivative, the compound of the following (i) and (ii) can use it as a cross linking agent.

(i) Compound which has N-hydroxymethyl group, an N-alkoxy methyl group, or N-acyloxy methyl group (ii)

Epoxy compound [0106] A cross linking agent is preferably used with 5 - 50% of the weight of an addition three to 65% of the weight among [all] resist constituent solid content. If a remaining rate of membrane falls that the addition of a cross linking agent is less than 3 % of the weight and 65 % of the weight is exceeded, resolving power declines and it is not so more desirable still in respect of the stability at the time of preservation of resist liquid.

[0107] In addition to the above-mentioned phenol derivative, in this invention, other above cross linking agents (i) and (ii) can also be used together. the ratio of other cross linking agents which can be used together in addition to the above-mentioned phenol derivative -- a mole ratio -- 100 / 0 - 20/80 -- desirable -- 90 / 10 - 40/60 -- it is 80 / 20 - 50/50 still more preferably.

[0108] These cross linking agents are explained below at a detail.

(i) As a compound which has N-hydroxymethyl group, an N-alkoxy methyl group, or N-acyloxy methyl group, the benzoguanamine-formaldehyde condensate indicated by the urea-formaldehyde condensate, the alkoxy substituted compound indicated at EP-A No. 0,212,482 is mentioned to the monomer and oligomer-melamine-formaldehyde condensate list indicated by the Europe patent public presentation (it is hereafter indicated as "EP-A") No. 0,133,216, the West German patent No. 3,634,671, and 3,711,264.

Furthermore, as a desirable example, the melamine-formaldehyde derivative which has at least two isolation N-hydroxymethyl groups, an N-alkoxy methyl group, or N-acyloxy methyl group is mentioned, for example, and especially an N-alkoxy methyl derivative is desirable especially.

[0109] (ii) As an epoxy compound, the epoxy compound of the shape of the monomer and dimer containing one or more epoxy groups, oligomer, and a polymer can be mentioned. For example, the resultant of bisphenol A and epichlorohydrin, the resultant of low-molecular-weight phenol-formaldehyde resin and epichlorohydrin, etc. are mentioned. In addition, the epoxy resin which is indicated by a U.S. Pat. No. 4,026,705 official report and the British patent No. 1,539,192 official report, and is used for them can be mentioned.

[0110] (4) As a compound which has the unsaturated bond which can carry out a polymerization by the acid and/or radical which are generated from the compound of compound this invention (A) which has the unsaturated bond in which a polymerization is possible by the acid and/or radical of this invention (E), the well-known monomer which has a polymerization nature machine can use it without a limit especially. Specifically as such a monomer, it is the compound which replaced monofunctional acrylic ester and its derivative, or these acrylate, such as 2-ethylhexyl acrylate, 2-hydroxyethyl acrylate, and 2-hydroxypropyl acrylate, with methacrylate, itaconate, crotonate, maleate, etc.;

[0111] Compound which replaced 2 organic-functions acrylic ester and its derivative, or these acrylate, such as polyethylene-glycol diacrylate, pentaerythritol diacrylate, bisphenol A diacrylate, and diacrylate of epsilon-caprolactone addition product of hydroxy pivalate neopentyl glycol, with methacrylate, itaconate, crotonate, maleate, etc.;

[0112] Or the compound which replaced polyfunctional acrylic ester and its derivative, or these acrylate, such as TORIMECHI roll pro pantry (meta) acrylate, dipentaerythritol pentaacrylate, dipentaerythritol hexaacrylate, and a pyrogallol thoria chestnut rate, with methacrylate, itaconate, crotonate, maleate, etc. can be mentioned. Moreover, an acrylic acid or methacrylic acid is introduced into the oligomer of suitable molecular weight, and what is called the so-called prepolymer which gave photopolymerization nature can be used suitably.

[0113] In addition, the compound of a publication etc. can be mentioned to JP,58-212994,A, 61-6649, 62-46688, 62-48589, 62-173295, 62-187092, 63-67189, JP,1-244891,A, etc., and the compound of the compound of "chemistry goods of 11290" Chemical Daily and a 286-294-page publication, a "UV-EB hardening handbook (volume on raw material)" macromolecule publication meeting, and a 11-65-page publication etc. can be used further suitably.

[0114] Especially, the compound which has two or more acrylic radicals or methacrylic radicals in intramolecular is desirable in this invention, and 5,000 or less thing has [10,000 or less] more preferably more desirable still molecular weight. In this invention, out of the monomer and prepolymer which have polymerization nature machines also including said illustrated thing, a polymerization nature compound can be used combining two or more sorts, if there is no problem in one sort or compatibility, and compatibility according to the purpose. the compound which has a partial saturation radical -- all the inside of resist constituent solid content -- it is preferably used with 10 - 30% of the weight of an addition still more preferably five to 40% of the weight two to 50% of the weight.

[0115] (5) Melt the negative-resist constituent of solvent this invention of this invention (D) to the solvent which dissolves each above-mentioned component, and apply it on a base material. In this invention, the solvent further shown in the following other than the solvent of (a) of (D) and (b) may be mixed suitably if needed. As a solvent to mix, ethylene dichloride, a cyclohexanone, Cyclopentanone, gamma-butyrolactone, a methyl ethyl ketone, methyl amyl ketone, Methyl isobutyl ketone, octanone 3, ethylene glycol monomethyl ether, Ethylene glycol monoethyl ether, 2-methoxy ethyl acetate, Ethylene glycol monoethyl ether acetate, toluene, ethyl acetate, Propyl acetate, isopropyl acetate, butyl acetate, isobutyl acetate, methyl lactate, Ethyl lactate, lactic-acid propyl, butyl lactate, methyl pyruvate, pyruvic-acid ethyl, Pyruvic-acid propyl, N.N-dimethylformamide, N,N-dimethylacetamide, Dimethyl sulfoxide, N and N, N', N'-tetramethyl urea, It is desirable, and these solvents may be added to (D), and N-methyl pyrrolidone, a tetrahydrofuran, ethylene carbonate, propylene carbonate, beta-methoxy isobutyric-acid methyl, ethyl butylate, at least one sort of butanoic acid propyls, etc. may be mixed, and may use them.

[0116] Also in the above, gamma-butyrolactone, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monoethyl ether acetate, N-methyl pyrrolidone, methyl amyl ketone, octanone 3, butyl acetate, isobutyl acetate, methyl pyruvate, pyruvic-acid ethyl, and a tetrahydrofuran can be mentioned as a desirable solvent mixed to the solvent of (a) of (D), and (b). The amount of solvents used other than (a) of (D) and (b) is 0 - 30 % of the weight preferably zero to 50% of the weight to all solvents.

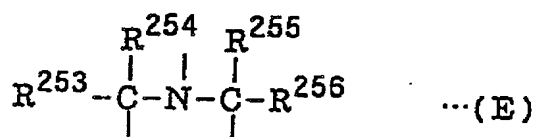
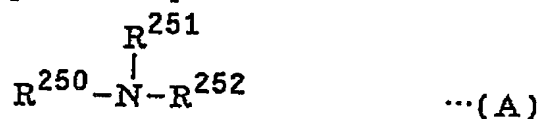
[0117] (6) The negative-resist constituent of component this invention of others which are used for the constituent of this invention can be made to contain a radical generating agent, an organic base nature compound, a color, a surfactant, etc. further if needed.

[0118] (6) -1 a color -- there are fat dye and basic dye as a suitable color. Specifically, oil yellow #101, oil yellow #103, oil pink #312, the oil green BG, oil blue BOS, oil blue #603, oil black BY, oil black BS, oil black T-505 (above the ORIENT chemical-industry incorporated company make), a crystal violet (CI42555), Methyl Violet (CI42535), rhodamine B (CI45170B), Malachite Green (CI42000), a methylene blue (CI52015), etc. can be mentioned.

[0119] (6) -2 The desirable organic base nature compound which can be used by organic base nature compound this invention is a compound with basicity stronger than a phenol. A nitrogen-containing basicity compound is desirable especially. As desirable chemical environment, the structure of following type (A) - (E) can be mentioned.

[0120]

[Formula 29]



[0121] Here, it is R250 and R251. And R252 may be the same, or you may differ, and the permutation of a hydrogen atom, the alkyl group of 1-6 carbon numbers, the amino alkyl group of 1-6 carbon numbers, the hydroxyalkyl radical of 1-6 carbon numbers, or 6-20 carbon numbers or an unsubstituted aryl group is expressed, it may join together mutually and R251 and R252 may form a ring here. R253, R254, and R255 And R256 may be the same, or may differ and expresses the alkyl group of 1-6 carbon numbers. Furthermore, a desirable compound is a nitrogen-containing basicity compound which has two or more nitrogen atoms of different chemical environment in a monad, and is a compound which has especially a compound or alkylamino radical including both ring structures containing the amino group and nitrogen atom which are not permuted [a permutation or] preferably.

[0122] As a desirable example, the aminopyridine which is not permuted [the guanidine which is not

permuted / a permutation or / a permutation, or], The amino pyrrolidine which is not permuted [the amino alkyl pyridine which is not permuted / a permutation or / a permutation, or], The pyrazole which is not permuted [the indazole which is not permuted / a permutation or /, an imidazole, a permutation, or], The pyrimidine which is not permuted [the pyrazine which is not permuted / a permutation or /, a permutation, or], The amino alkyl morpholine which is not permuted [the amino morpholine which is not permuted / the piperazine which is not permuted / the pyrazoline which is not permuted / the imidazoline which is not permuted / the pudding which is not permuted / a permutation or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or] is mentioned. Desirable substituents are the amino group, an amino alkyl group, an alkylamino radical, an amino aryl group, an arylamino radical, an alkyl group, an alkoxy group, an acyl group, an acyloxy radical, an aryl group, an aryloxy group, a nitro group, a hydroxyl group, and a cyano group.

[0123] As a desirable compound, especially Guanidine, 1, and 1-dimethyl guanidine, 1, 1, 3, 3, - tetramethyl guanidine, an imidazole, 2-methylimidazole, 4-methyl imidazole, N-methyl imidazole, 2-phenylimidazole, 4, 5-diphenyl imidazole, 2 and 4, 5-triphenyl imidazole, 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, 2-dimethylamino pyridine, 4-dimethylaminopyridine, 2-diethylamino pyridine, 2-(aminomethyl) pyridine, 2-amino-3-methylpyridine, 2-amino-4-methylpyridine, 2-amino-5-methylpyridine, 2-amino-6-methylpyridine, 3-aminoethyl pyridine, 4-aminoethyl pyridine, [0124] 3-amino pyrrolidine, a piperazine, N-(2-aminoethyl) piperazine, N-(2-aminoethyl) piperidine, 4-amino - 2, 2, 6, and 6-tetramethylpiperidine, 4-piperidino piperidine, a 2-imino piperidine, 1-(2-aminoethyl) pyrrolidine, A pyrazole, 3-amino-5-methyl pyrazole, 5 - Amino-3-methyl-1-p-tolyl pyrazole, Pyrazine, 2-(aminomethyl)-5-methyl pyrazine, a pyrimidine, Although 2, 4-diamino pyrimidine, 4, 6-dihydroxy pyrimidine, 2-pyrazoline, 3-pyrazoline, N-amino morpholine, N-(2-aminoethyl) morpholine, etc. are mentioned, it is not limited to this. These nitrogen-containing basicity compounds are independent, or are used together two or more sorts.

[0125] As for the operating rate in the constituent of an acid generator and an organic base nature compound, it is desirable that it is a (acid generator) / (organic base nature compound) (mole ratio) = 2.5-300. This mole ratio may serve as low sensibility less than by 2.5, resolving power may decline, and if 300 is exceeded, **** of a resist pattern may become large by the passage of time to exposure afterbaking processing, and resolving power may also decline. a (acid generator) -- / (organic base nature compound) (mole ratio) -- desirable -- 5.0-200 -- it is 7.0-150 still more preferably.

[0126] (6) -3 Since the negative-resist constituent of radical generating agent this invention is made to promote the reaction of the polymerization nature compound of (D) if needed, a radical generating agent can be used together. There is no limit especially about the well-known radical polymerization initiator generally used for the giant-molecule composition reaction by the radical polymerization as such a radical generating agent. It can be used. Azobis nitril system compounds, such as - azobisisobutyronitril, and 2 and 2 '2, 2'-azobis propionitrile, A benzoyl peroxide, lauroyl peroxide, an acetyl peroxide, perbenzoic-acid-t-butyl, alpha-cumyl hydronalium peroxide, di-t-butyl peroxide, Organic peroxide, such as diisopropyl peroxi dicarbonate, t-butylperoxyisopropylcarbonate, peroxy acids, alkyl peroxy carbamates, and nitroso aryl acyl amines, [0127] Inorganic peroxides, such as potassium persulfate, ammonium persulfate, and a potassium perchlorate, Diazoaminobenzene, p-nitrobenzene diazonium, and azobis permutation alkanes Azo or diazo

compounds, such as diazo thioether and arylazo sulfones, Tetra-alkyl thiuram disulfide, such as a nitroso phenyl urea and tetramethylthiuramdisulfide Diaryl disulfide, such as dibenzoyl disulfide, dialkyl xanthogenic acid disulfide, aryl sulfinic acids, arylated alkyl sulfones, and 1-alkane sulfinic acids can be mentioned.

[0128] As for the activation energy for radical generating of a radical generating agent, it is desirable that they are 30Kcal(s)/more than a mol, and an azobis nitril system compound and organic peroxide are mentioned as such a thing. Especially, it excels in stability in ordinary temperature, and the catabolic rate at the time of heating is quick, the compound which serves as colorlessness at the time of decomposition is desirable, and benzoyl-peroxide, 2, and 2'-azobisisobutyronitril etc. can be mentioned. The above-mentioned radical generating agent may be used independently, or may be used together two or more sorts, and is preferably used at 2 - 10 % of the weight about 0.5 to 30% of the weight to the total solids of a radical polymerization layer.

[0129] (6) -4 A surfactant can also be added to the surfactants above-mentioned solvent. Specifically The polyoxyethylene lauryl ether, polyoxyethylene stearylether, Polyoxyethylene alkyl ether, such as the polyoxyethylene cetyl ether and the polyoxyethylene oleyl ether Polyoxyethylene alkyl aryl ether, such as the polyoxyethylene octyl phenol ether and the polyoxyethylene nonyl phenol ether Polyoxyethylene polyoxypropylene block copolymers Sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, Sorbitan fatty acid esters, such as sorbitan monooleate, sorbitan trioleate, and sorbitan tristearate Polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, The Nonion system surfactants, such as polyoxyethylene sorbitan fatty acid ester, such as polyoxyethylenesorbitan monostearate, polyoxyethylene sorbitan trioleate, and polyoxyethylene sorbitan tristearate, can be mentioned.

[0130] As these surfactants, furthermore, for example, JP,62-36663,A, JP,61-226746,A, JP,61-226745,A, JP,62-170950,A, JP,63-34540,A, JP,7-230165,A, JP,8-62834,A, JP,9-54432,A, JP,9-5988,A, a U.S. Pat. No. 5405720 number, said -- No. 5360692 -- said -- No. 5529881 -- said -- No. 5296330 -- said -- No. 5436098 -- said -- No. 5576143 -- said -- a surfactant No. 5294511 and given [this] in No. 5824451 can be mentioned, and the surfactant of the following marketing can also be used as it is. As a surfactant of marketing which can be used, for example, EFUTOPPU EF301, EF303, and EF352 (new Akita formation Make), The megger fucks F171 and F173 (Dainippon Ink make), Fluorad FC430 and FC431 (Sumitomo 3M make), The Asahi guard AG710, Sir chlorofluocarbon S-382, SC101, SC102, SC103, SC104, SC105, SC106 (Asahi Glass Co., Ltd. make), Fluorochemical surfactants, such as Troysol S-366 (made in Troy Chemical), Organosiloxane polymer KP341 (Shin-Etsu Chemical Co., Ltd. make), an acrylic-acid system or methacrylic-acid system (**) polymerization poly flow No.75, No.95 (product made from Kyoeisha Fats-and-oils Chemical industry), etc. can be mentioned.

[0131] The loadings of these surfactants are usually 0.01 % of the weight - 1 % of the weight preferably 0.001 % of the weight to 2% of the weight on the basis of the solid content in all the constituents of this invention. You may add independently and these surfactants can also be added in some combination.

[0132] In manufacture of a precision integrated circuit device etc. the pattern formation process to a resist film top On substrates (example: transparence substrates, such as silicon / diacid-ized silicon leather **, a glass substrate, and an ITO substrate etc.) The negative-mold photoresist constituent of this invention can be applied, it can irradiate by the ability using an electron ray (under the acceleration voltage condition of 75

or more keVs), or X drawing drawing equipment next, and a good resist pattern can be formed heating, development, a rinse, and by drying.

[0133] As a developer of the negative-mold photoresist constituent of this invention A sodium hydroxide, a potassium hydroxide, a sodium carbonate, a sodium silicate, Inorganic alkali, such as a meta-sodium silicate and aqueous ammonia, ethylamine, Secondary amines, such as primary amines, such as n propylamine, diethylamine, and G n butylamine Tertiary amines, such as triethylamine and methyl diethylamine, dimethylethanolamine, The water solution of alkali, such as annular amines, such as quarternary ammonium salt, such as alcoholic amines, such as a TORIETA no amine, tetramethylammonium hydroxide, tetraethylammonium hydroxide, and a choline, a pyrrole, and a piperidine, can be used. Furthermore, surfactants, such as alcohols, such as isopropyl alcohol, and the Nonion system, can also be used for the water solution of the above-mentioned alkali, carrying out suitable amount addition. the inside of these developers -- desirable -- quaternary ammonium salt -- they are tetramethylammonium hydroxide and a choline still more preferably.

[0134]

[Example] Hereafter, although an example explains this invention to a detail further, thereby, the contents of this invention are not limited.

[0135] 1. Example 1 (Composition of Example of Resin (2)) of Alkali Fusibility Resin Composition Which Has Partial Saturation Radical in which Synthetic Example (1) Polymerization of Configuration Material is Possible

Pori (4-hydroxystyrene) (Nippon Soda Co., Ltd. make, trade name VP-15000) 12.1g (0.10 mols) was dissolved in THF100ml, and 3.7g (0.024 mols) of methacrylic-acid anhydrides was added. Furthermore, pyridine 2.4g (0.030 mols) was added and heating reflux was carried out for bottom 5 hours of stirring. White resin was deposited by supplying stirring violently in [after cooling reaction mixture radiationally] ion-exchange-water 1L. With ion exchange water, the obtained resin was dried under reduced pressure after rinsing, and resin (2)13.1g of this invention was obtained. When the content of a partial saturation radical was measured by NMR, the amount of installation of the methacrylic radical to the OH radical of polyhydroxy styrene was 18-mol %. Moreover, when molecular weight was measured in GPC, it was 16,700 (degree of dispersion 1.2; polystyrene criterion) in the weighted mean.

[0136] The synthetic example 2 (composition of the example of resin (4))

Pori (4-hydroxystyrene) (Nippon Soda Co., Ltd. make, trade name VP-8000) 12.1g (0.10 mols) is dissolved in 100ml of N,N-dimethylacetamide, and it is 2-isocyanato ethyl to this. Methacrylate 3.1g (0.020 mols) was added and it heated at 90 degrees C under stirring for 7 hours. White resin was deposited by supplying stirring violently in [after cooling reaction mixture radiationally] ion-exchange-water 1L. With ion exchange water, the obtained resin was dried under reduced pressure after rinsing, and resin (4)14.4g of this invention was obtained. When the content of a partial saturation radical was measured by NMR, the amount of installation of the methacrylic radical to the OH radical of polyhydroxy styrene was 16-mol %. Moreover, when molecular weight was measured in GPC, it was 9,100 (degree of dispersion 1.2; polystyrene criterion) in the weighted mean.

[0137] The synthetic example 3 (composition of the example of resin (7))

Pori (4-hydroxystyrene) (Nippon Soda Co., Ltd. make, trade name VP-8000) 12.1g (0.10 mols) was dissolved

in THF 100ml, and 4-styrene sulfonyl chloride 4.7g (0.023 mols) was added. Furthermore, it was dropped under ice-cooling of N and a THF 20ml solution (N-dimethylamino pyridine 0.37g (0.003 mols) / triethylamine 2.1g (0.020 mols)), stirring. Furthermore, it stirred under the room temperature for 5 hours. White resin was deposited by supplying filtering reaction mixture and stirring filtrate violently in ion-exchange-water 1L. With ion exchange water, the obtained resin was dried under reduced pressure after rinsing, and resin (7) 15.0g of this invention was obtained. When the content of a partial saturation radical was measured by NMR, the amount of installation of the styryl radical to the OH radical of polyhydroxy styrene was 18-mol %. Moreover, when molecular weight was measured in GPC, it was 9,200 (degree of dispersion 1.2; polystyrene criterion) in the weighted mean.

[0138] The synthetic example 4 (composition of ***** (8))

Pori (4-hydroxystyrene) (Nippon Soda Co., Ltd. make, trade name VP-8000) 12.1g (0.10 mols) was dissolved in 100ml of N,N-dimethylacetamide, and chloro methyl styrene 3.4g (0.022 mols) was added to this. Furthermore, triethylamine 2.3g (0.022 mols) 20ml solution of N,N-dimethylacetamide was dropped under the room temperature, agitating. Reaction mixture was agitated at 60 degrees C after that for 5 hours. White resin was deposited by supplying stirring violently in [after cooling reaction mixture radiationally] ion-exchange-water 1L. With ion exchange water, the obtained resin was dried under reduced pressure after rinsing, and resin (8) 13.9g of this invention was obtained. When the content of a partial saturation radical was measured by NMR, the amount of installation of the styryl radical to the OH radical of polyhydroxy styrene was 17-mol %. Moreover, when molecular weight was measured in GPC, it was 9,300 (degree of dispersion 1.2; polystyrene criterion) in the weighted mean. Hereafter, the resin of this invention (B) was compounded similarly.

[0139] (2) Synthetic pen TAFUORO benzenesulphonyl chloride 25g of an acid generator 1 Pentough Rollo benzenesulfonic acid tetramethylammonium salt was dissolved in bottom methanol of ice-cooling 100ml, and 100g of tetramethylammonium hydroxide water solutions was slowly added to this 25%. When stirred at the room temperature for 3 hours, the solution of the Pentough Rollo benzenesulfonic acid tetramethylammonium salt was obtained. This solution was used for the salt exchange with sulfonium salt and iodonium salt.

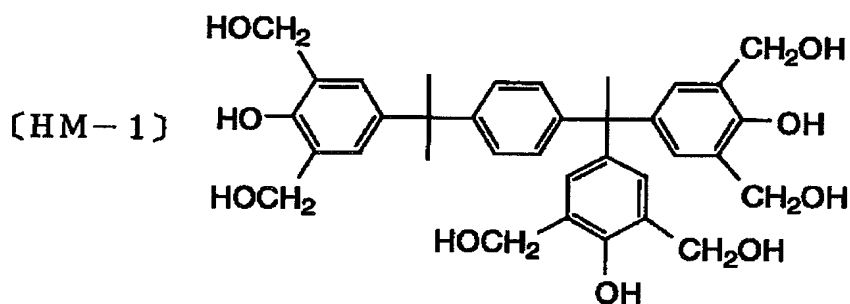
[0140] 2) Synthetic diphenyl sulfoxide 50g of triphenylsulfonium Pentough ROROBENZEN sulfonate was dissolved in benzene 800ml, 200g of aluminum chlorides was added to this, and it flowed back for 24 hours. Ice 2L was slowly filled with reaction mixture, 400ml of concentrated hydrochloric acid was added to this, and it heated at 70 degrees C for 10 minutes. After washing and filtering this water solution by 500ml of ethyl acetate, what dissolved 200g of ammonium iodide in 400ml of water was added. When ethyl acetate washed after rinsing, **** and, and the fine particles which deposited were dried, 70g of triphenylsulfonium iodide was obtained. Triphenylsulfonium iodide 30.5g was dissolved in methanol 1000ml, 19.1g of silver oxides was added to this solution, and it stirred at the room temperature for 4 hours. The solution was filtered and the solution of the Pentough Rollo benzenesulfonic acid tetramethylammonium salt of an excessive amount was added to this. Reaction mixture was condensed, this was dissolved in dichloromethane 500ml, and a tetramethylammonium hydroxide water solution and water washed this solution 5%. When the organic phase was condensed after desiccation with anhydrous sodium sulfate, triphenylsulfonium Pentough ROROBENZEN sulfonate (I-1) was obtained.

[0141] 3) Synthetic t-amyl benzene 60g [of JI (4-t-amyl phenyl) iodonium Pentough ROROBENZEN sulfonate], 39.5g [of potassium iodates], 81g [of acetic anhydrides], and dichloromethane 170ml was mixed, and 66.8g of bottom concentrated sulfuric acid of ice-cooling was slowly dropped at this. After stirring under ice-cooling for 2 hours, it stirred at the room temperature for 10 hours. 500ml of water was added to reaction mixture under ice-cooling, and when it condensed after it washed this by dichloromethane and a sodium hydrogencarbonate and water washed the extract and the organic phase, the JI (4-t-amyl phenyl) iodonium sulfate was obtained. This sulfate was added to the solution of the Pentough Rollo benzenesulfonic acid tetramethylammonium salt of an excessive amount. 500ml of water was added to this solution, and when it condensed after it washed this by dichloromethane and a tetramethylammonium hydroxide water solution and water washed the extract and the organic phase 5%, JI (4-t-amyl phenyl) iodonium Pentough ROROBENZEN sulfonate (III-1) was obtained. It is compoundable using the same approach as the above also about other compounds.

[0142] (3) Synthetic 1-[alpha-methyl-alpha-(4-hydroxyphenyl) ethyl]-4-[alpha and alpha-bis(4-hydroxyphenyl) ethyl] benzene 20g (Trisp-PA by Honshu Chemical Industry Co., Ltd.) of a cross linking agent cross linking agent [HM-1] was moreover agitated and dissolved in 10% potassium-hydroxide water solution. Next, 60ml of formalin aqueous solution was gradually added over 1 hour under the room temperature 37%, stirring this solution. After stirring under a room temperature furthermore for 6 hours, it acted to the dilute-sulfuric-acid water solution as ** people. After filtering the sludge and rinsing enough, 20g of white powder of phenol derivative [HM-1] which has the hydroxymethyl group of the following structure was obtained by recrystallizing from methanol 30ml. Purity was 92% (liquid chromatography method).

[0143]

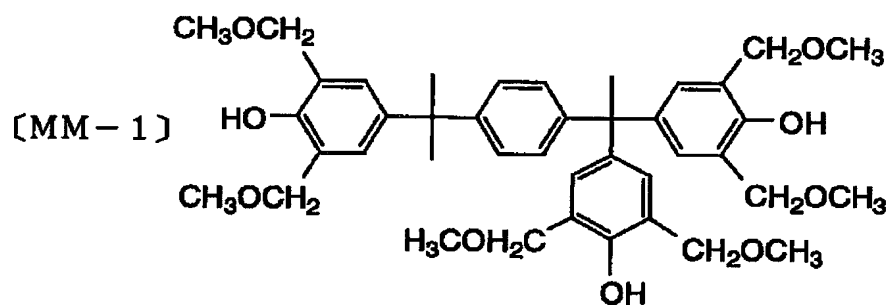
[Formula 30]



[0144] Phenol derivative [HM-1] 20g which has the hydroxymethyl group obtained in the example of the synthetic above-mentioned composition of a cross linking agent [MM-1] was added to the 1l. methanol, and carried out heating churning, and it dissolved. Next, 1ml of concentrated sulfuric acid was added to this solution, and heating reflux was carried out for 12 hours. Reaction mixture was cooled after reaction termination and potassium carbonate 2g ** was added. After condensing this mixture enough, 300ml of ethyl acetate was added. After rinsing this solution, 22g of white solid-states of the phenol derivative [MM-1] which has the methoxymethyl radical of the following structure was obtained by carrying out concentration hardening by drying. Purity was 90% (liquid chromatography method).

[0145]

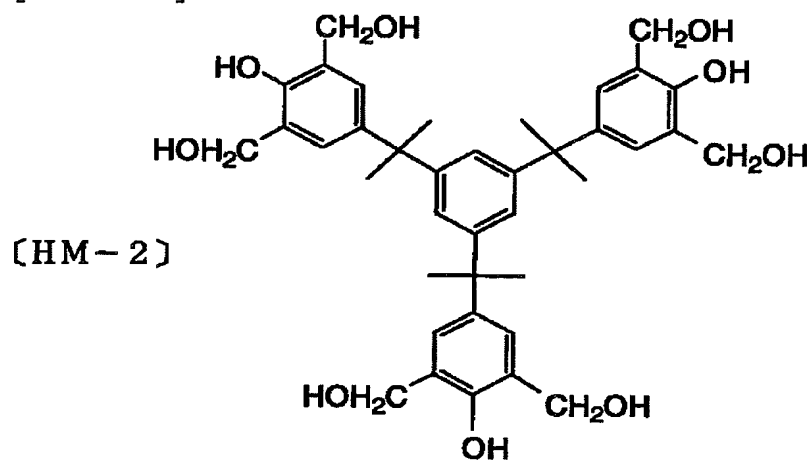
[Formula 31]



[0146] Furthermore, the phenol derivative shown below similarly was compounded.

[0147]

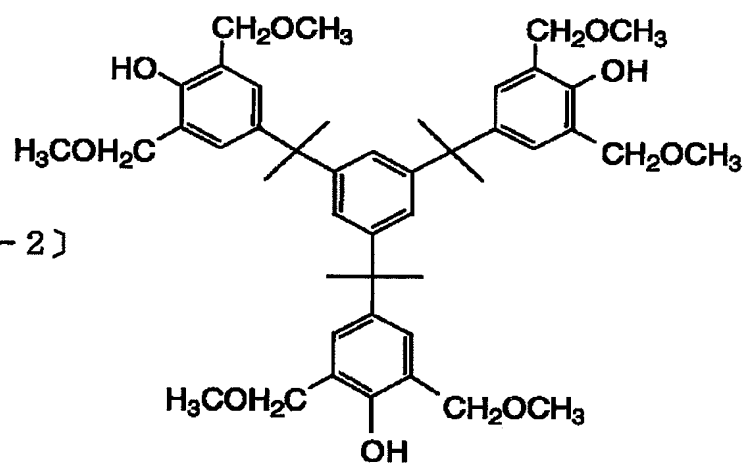
[Formula 32]



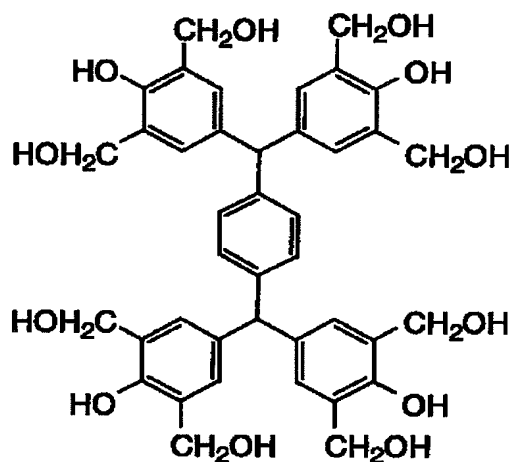
[0148]

[Formula 33]

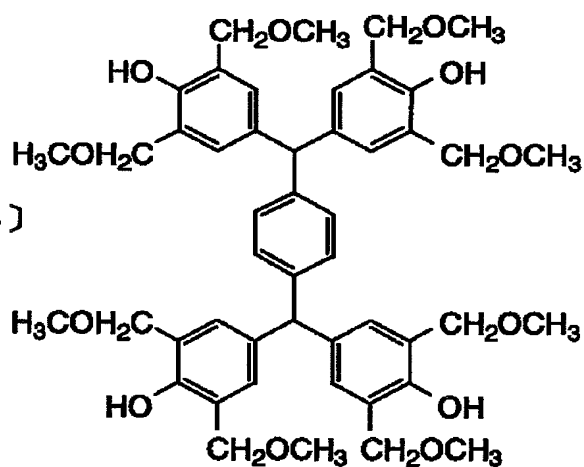
[MM-2]



[HM-3]

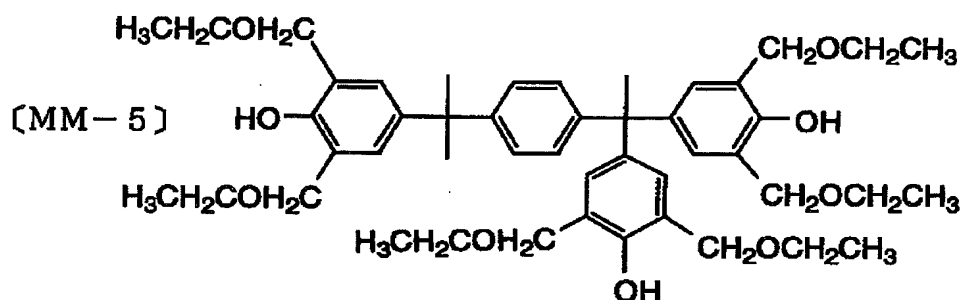
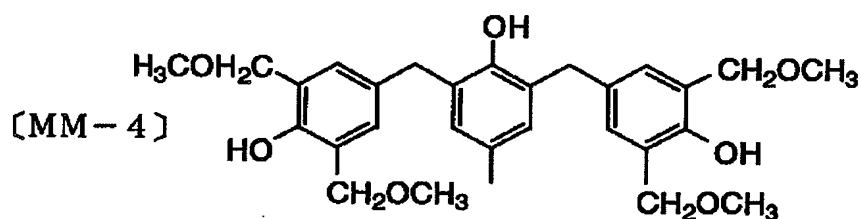
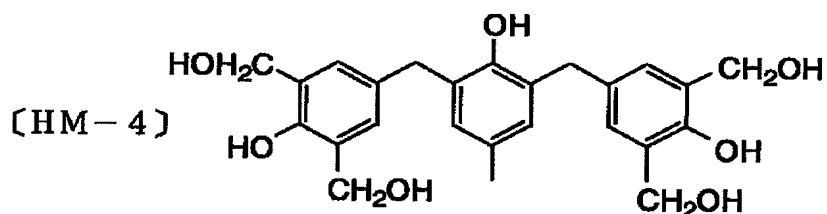


[MM-3]



[0149]

[Formula 34]



2. Example [Example and Example of Comparison]

(1) The solution of the photoresist constituent of the presentation shown in the following table 1 was adjusted using the compound and the compound for a comparison which constitute this invention chosen from the synthetic example of the painting above of a resist. After filtering each sample solution with a 0.1-micrometer filter, using the spin coater, it applied on the silicon wafer, and for 110 degrees C and 90 seconds, it dried with the hot plate of a vacuum adsorption mold, and the resist film of 0.3 micrometers of thickness was obtained.

[0150]

[Table 1]

表-1

| | 樹脂(g) | 酸発生剤(g) | 架橋剤(g) | 溶剤(g) | 重合性 モノマー(g) |
|--------|--------------------|--------------|-------------|-------------------|----------------|
| 実施例 1 | (2) (1.05) | I-1 (0.07) | MM-1 (0.18) | a1/b1 = 8/2 (8.5) | なし |
| 実施例 2 | (4) (1.05) | I-8 (0.07) | MM-3 (0.18) | a1/b1 = 7/3 (8.5) | なし |
| 実施例 3 | (7) (1.05) | I-9 (0.07) | MM-4 (0.18) | a2/b1 = 7/3 (8.5) | なし |
| 実施例 4 | (8) (1.05) | II-1 (0.07) | MM-2 (0.18) | a1/b2 = 8/2 (8.5) | なし |
| 実施例 5 | (15) (1.05) | II-4 (0.07) | CL-1 (0.18) | a1/b3 = 8/2 (8.5) | なし |
| 実施例 6 | (20) (1.05) | III-1 (0.07) | MM-1 (0.18) | a2/b2 = 7/3 (8.5) | なし |
| 実施例 7 | (26) (1.05) | III-2 (0.07) | MM-2 (0.18) | a3/b2 = 6/4 (8.5) | RM-1 (0.12) |
| 実施例 8 | (28) (1.05) | I-1 (0.07) | MM-3 (0.18) | a1/b1 = 7/3 (8.5) | RM-2 (0.12) |
| 実施例 9 | (40) (1.05) | II-1 (0.07) | CL-2 (0.18) | a2/b1 = 7/3 (8.5) | RM-3 (0.12) |
| 実施例 10 | (47) (1.05) | III-2 (0.07) | MM-1 (0.18) | a1/b3 = 8/2 (8.5) | なし |
| 実施例 11 | (58) (1.05) | I-9 (0.07) | CL-1 (0.18) | a3/b2 = 6/4 (8.5) | RM-1 (0.12) |
| 実施例 12 | (59) (1.05) | PAG-1 (0.07) | MM-1 (0.18) | a1/b1 = 8/2 (8.5) | RM-3 (0.12) |
| 比較例 1 | (1.05) Polymer1 | PAG-1 (0.07) | CL-1 (0.28) | a1 (8.5) | なし |
| 比較例 2 | (1.05) Polymer2 | I-1 (0.07) | MM-1 (0.30) | a1 (8.5) | なし |

[0151] For the presentation of resin (40), the presentation of x/y/z=82/13/5 and resin (47) was [the resin of x/y/z=65/20/15 and others of the presentation of x/y/z=78/15/7, resin (58), and (59)] x/y=80 / 20 - 85/15 in the preparation ratio among Table 1, and the range of each weight average molecular weight was 8,000-16,000 (degree of dispersion 1.2-2.4).

[0152] <Resin> Polymer 1: Pori (4-hydroxystyrene) (Nippon Soda [Co., Ltd.] make: VP-8000)

Polymer2: Pori (3-hydroxystyrene) (Maruzen Petrochemical [Co., Ltd.] make: Mw=9700, Mw/Mn=2.2)

[0153]

[Formula 35]

< 光酸発生剤 >

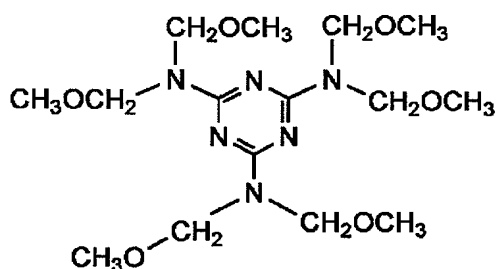


[0154]

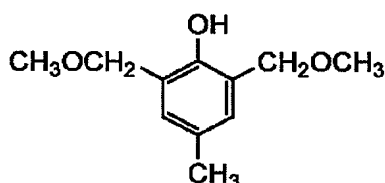
[Formula 36]

(架橋剤)

GL-1:



GL-2:



[0155] As a polymerization nature monomer, it is RM-1:tetraethylene glycol diacrylate (Nippon Kayaku Co., Ltd. make).

RM-2: Trimethylolpropane triacrylate (Nippon Kayaku Co., Ltd. make)

RM-3: Dipentaerythritol hexaacrylate (Nippon Kayaku Co., Ltd. make)

*****.

[0156] As a solvent, a1:propylene-glycol-monomethyl-ether acetate a2:3-methoxy methyl propionate a3:3-methoxy ethyl propionate b1:propylene-glycol-monomethyl-ether b2:ethyl lactate b3:diacetone alcohol is expressed.

[0157] (2) The resist film of ***** of a resist pattern was irradiated by using electron-beam-lithography equipment (acceleration voltage 50KeV). The 110-degree C vacuum adsorption mold hot plate performed heating for 60 seconds after the exposure, respectively, and it was immersed for 60 seconds in the tetramethylammonium hydroxide (TMAH) water solution 2.38%, and for 30 seconds, with water, the rinse was carried out and it dried. The cross-section configuration of the obtained pattern was observed with the scanning electron microscope. Moreover, sensibility made sensibility the minimum exposure energy when resolving 0.20-micrometer Rhine (Rhine: tooth-space =1:1), and made resolution marginal resolution (Rhine and a tooth space are separation resolving) in the exposure. Resolution of the thing which 0.20-micrometer Rhine (Rhine: tooth-space =1:1) does not resolve, therefore a limitation was made into resolution, and exposure energy at that time was made into sensibility. A development defect, spreading nature, and solvent solubility are the followings, and were made and evaluated.

[0158] [The number of development defects]: About the resist pattern obtained as mentioned above, the number of development defects was measured by KLA-2112 Made from a KEERUE ten call opportunity, and the acquired primary data value was made into the number of development defects.

[0159] [Spreading nature (homogeneity within a field)]: Each resist solution was applied on the 8 inch silicon wafer, the same processing as painting of the above resist layers was performed, and the resist spreading

film for the homogeneity measurement within a field was obtained. In LambdaA by great Japan screen incorporated company, 36 of these were equally measured so that it might become a cross joint along the wafer diameter direction about spreading thickness. The standard deviation of each measured value was taken and O and 50 or more things were evaluated for that with which the 3 times do not fill 50 as x.

[0160] [Solvent solubility]: Particle initial value and the number of increments of the particle after preservation with the passage of time estimated solvent solubility.

The number of particle in liquid after leaving it for one week at 25 degrees C immediately after preparation (particle initial value) about the positive type photoresist constituent solution (coating liquid) prepared as mentioned above (the number of particle after the passage of time) was counted at the Rion make and a particle counter. The number of the increments in particle calculated with particle initial value by $-(\text{the number of particle after the passage of time}) (\text{particle initial value})$ was evaluated. In addition, size of measurement particle was set to 0.3 micrometers or more.

[0161] The performance-evaluation result was shown in Table 2.

[0162]

[Table 2]

表-2

| | 感度 ($\mu\text{C}/\text{cm}^2$) | 解像力 (μm) | プロファイル | 現像欠陥数 | 塗布性 | パターニクル 初期値 | パターニクル 増加数 |
|--------|-------------------------------------|--------------------------|--------|-------|-----|---------------|---------------|
| 実施例 1 | 6 | 0.09 | 矩形 | 75 | ○ | 4 | 2 |
| 実施例 2 | 7 | 0.09 | 矩形 | 68 | ○ | 3 | 1 |
| 実施例 3 | 9 | 0.08 | 矩形 | 57 | ○ | 5 | 1 |
| 実施例 4 | 5 | 0.09 | 矩形 | 64 | ○ | 6 | 2 |
| 実施例 5 | 6 | 0.08 | 矩形 | 80 | ○ | 7 | 1 |
| 実施例 6 | 7 | 0.09 | 矩形 | 69 | ○ | 5 | 3 |
| 実施例 7 | 5 | 0.10 | 矩形 | 62 | ○ | 4 | 2 |
| 実施例 8 | 10 | 0.08 | 矩形 | 74 | ○ | 3 | 0 |
| 実施例 9 | 7 | 0.10 | 矩形 | 55 | ○ | 4 | 1 |
| 実施例 10 | 5 | 0.09 | 矩形 | 73 | ○ | 6 | 2 |
| 実施例 11 | 11 | 0.10 | 矩形 | 65 | ○ | 5 | 1 |
| 実施例 12 | 10 | 0.11 | 矩形 | 70 | ○ | 4 | 1 |
| 比較例 1 | 26 | 0.22 | ややテーパー | 445 | × | 20 | 25 |
| 比較例 2 | 20 | 0.20 | ややテーパー | 165 | × | 14 | 20 |

[0163] The result of Table 2 shows that the negative-resist constituent of this invention which combined the polymerization nature monomer is excellent in all compared with the example of a comparison without this component.

[0164] It irradiated on condition that the acceleration voltage of 75KeV to the resist film created like the above using electron-beam-lithography equipment using the presentation of the above-mentioned examples 1, 4, 7, and 12 and the example 1 of a comparison (examples 13-16, example 3 of a comparison). Heating, development, and a rinse were performed like the above-mentioned example after the exposure, and the obtained pattern was observed under the scanning electron ray microscope. The result similarly estimated as the above-mentioned example was shown in Table 3.

[0165]

[Table 3]

表-3

| | 感度 ($\mu\text{C}/\text{cm}^2$) | 解像力 (μm) | プロファイル | 現像欠陥数 | 塗布性 | パーティクル 初期値 | パーティクル 増加数 |
|--------|-------------------------------------|--------------------------|--------|-------|-----|---------------|---------------|
| 実施例 13 | 10 | 0.08 | 矩形 | 78 | ○ | 3 | 2 |
| 実施例 14 | 7 | 0.08 | 矩形 | 67 | ○ | 6 | 1 |
| 実施例 15 | 8 | 0.08 | 矩形 | 65 | ○ | 4 | 1 |
| 実施例 16 | 17 | 0.10 | 矩形 | 68 | ○ | 3 | 1 |
| 比較例 3 | 45 | 0.20 | ややテーパ- | 430 | × | 22 | 20 |

[0166] The result of Table 3 shows that the negative-resist constituent of this invention is excellent in all also in the electron beam irradiation in high acceleration voltage to the constituent of the example of a comparison.

[0167]

[Effect of the Invention] This invention can offer the negative-resist constituent which is excellent in sensibility and resolution, and makes a rectangle profile possible, and is excellent also in a development defect, spreading nature, and solvent solubility also in the conditions of high acceleration voltage.

[Translation done.]